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CARBON

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INDUSTRIAL CARBON

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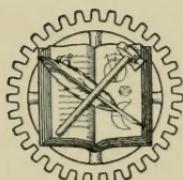
INDUSTRIAL CARBON

By

C. L. MANTELL, Ph.D.

Pratt Institute, Brooklyn

*Member, American Institute of Mining and
Metallurgical Engineers, American Institute
of Chemical Engineers*



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PREFACE

CARBON, in its industrial applications, is a subject which is at the same time very wide and very specialized. Its ramifications are many, and its forms numerous. Its technology is as yet young but its development in the last two decades has been so rapid as to be astounding.

The literature of carbon is widely scattered; in some phases it has been exceedingly sparse, in others plentiful, but at times paradoxical, at times contradictory, incomplete and biased. The literature on the carbon industries is only of recent development.

In preparing this book, the author has attempted to cover the technologic applications of elemental carbon, aside from its use as a fuel. The term "elemental carbon" is applied to mean those substances, materials and products which are either carbon in its elemental form, or which consist entirely of carbon, or whose value in industry is due to the physical and chemical properties of the elemental carbon from which they are made or which they contain. A chapter on charcoal as a fuel is included for reference in connection with the many applications of charcoal as an adsorbent, as well as for those who, especially interested in specific uses of adsorbent char, (such as a mining engineer in gold and silver work), may desire some information as to how charcoal is made on a commercial scale.

The possibility of expansion of the carbon industries is very great, for they are intimately bound up with our highly complex life of the present day.

The contents of this volume fall naturally into several subdivisions, — the truly elemental forms such as diamonds and graphites, with their industrial phases; carbon pigments and fillers, such as carbon black, lampblack and other blacks; adsorbent carbons of the gas, decolorizing and metal ad-

sorbent types, with which bone black is grouped; and the manufactured carbon products, such as electrodes, brushes, etc. A reference chapter on the physical characteristics of carbon is included.

The author has been truly fortunate in having been the recipient of much valuable aid from many actively engaged in phases of the carbon industries. He wishes to acknowledge the help of Mr. Jim Hanifen of the Van Itallie Co. and Mr. Edward Katz and Mr. Hirsch of the Diamond Drill Carbon Co. for their criticisms of the chapter on diamonds; Mr. Lyman Judson and Mr. E. C. Sprague of the Acheson Graphite Co. for their criticism of the sections on artificial graphite; Mr. J. H. Schermerhorn, Vice-president, Mr. Motion and Mr. Van Dorn of the Joseph Dixon Crucible Co. for their criticism of the sections on natural graphite, crucibles, lubricating graphite, foundry facings and graphite applications; Mr. Lewis H. Lawton of the Jonathan Bartley Crucible Co. for his criticism of the chapters on crucibles and graphite; Mr. G. C. Lewis of the L. Martin Co. for his criticism of the chapters on carbon black and the black pigments; Dr. Paul M. Horton of the Audubon Sugar School, Louisiana State University, for his criticism of the chapter on bone black; Mr. Leonard Wickenden, Vice-president, the Suchar Process Corporation, Mr. Bernard Glick of the Industrial Chemical Co., Mr. L. M. Gill and Mr. Herr of the Darco Sales Corporation for their advice and criticisms of the chapter on decolorizing carbon; Mr. A. W. Allen, Editor, Engineering and Mining Journal, for his review of the metal adsorbent char section; Mr. Frank J. Vosburg, Electrode Sales Division, National Carbon Co., for his criticism of the electrode sections; Mr. M. Sem, American representative of Det Norske Aktieselskab for Electroke-misk Industri for aid in connection with Söderberg electrodes; Mr. H. S. Conrad, Vice-president of the Stackpole Carbon Co., for aid in reference to carbon brushes; all of which has been gratefully received and has been incorporated in the text. This volume is thus the result, not of the

labors of one, but of the combined efforts of many workers in the field. Last but not least, the author wishes to acknowledge the invaluable assistance of his co-workers, Mr. Andrew Hathaway, who made the drawings for the illustrations, and Miss Edna M. Rogers, who painstakingly prepared the manuscript.

For the use of photographs and illustrations, the author is indebted to the Diamond Drill Carbon Co., the Van Itallie Co., the Acheson Graphite Co., Engineering and Mining Journal, Chemical and Metallurgical Engineering, the Jonathan Bartley Crucible Co., the Crossley Machine Co., the United States Bureau of Mines, the Joubert and Goslin Machine and Foundry Co., the Isbell Porter Co., the Suchar Process Corporation, the National Carbon Co., Det Norske Aktieselskab for Electrokemisk Industri, the John Robertson Co., the Stackpole Carbon Co., the Ohio Carbon Co., the Hydraulic Press Manufacturing Co. and the Watson Stillman Co.

It is hoped that this volume will be of help to the many investigators, workers, producers and consumers in the carbon industries. Criticisms will be welcomed at all times.

C. L. MANTELL.

PRATT INSTITUTE,
Brooklyn, N. Y.
October, 1928.

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CHAPTER I

INTRODUCTION

CARBON, in its elemental and allotropic forms, aside from its use as a fuel, plays a very important part in our every-day existence. Its value in industry may be better realized through the fact that carbon and its related products to the value of more than one hundred million dollars are produced annually in the United States. Due to its dirty habits and uncultured nature, carbon has often been in the step-child's position; as a result of its black, grimy outward appearance and its shy habits but very little attention has been paid to it in the literature.

Carbon is the only element which carried the Greek name "adamas" which means invincible. The diamond derives its name from this source. It has ranked as the leader among precious stones for centuries. It has been at various times credited with supernatural qualities. In the Middle Ages, the diamond was known as the peacemaker between husband and wife, which attribute still holds good. The diamond as a gem brings thoughts of untold romance, sorrow, struggles and riches. In its industrial forms, popularly known as black diamonds, it is one of the very few materials which man can use in boring drills for robbing the earth of its valuable oil and minerals. We meet it again in the every-day glazier's diamond glass cutter, or in diamond dies for drawing fine wires.

While the diamond is the hardest material known, its sister, graphite, an allotropic form of carbon, is one of the softest. Graphite makes the world roll on more smoothly, less noisily and less wearingly, a much-to-be-desired end in this world of rush and bustle,—for graphite is a lubricant

par excellence. Graphite is remarkably resistant to chemical attack under severe conditions. All our electrolytic industries, our caustic for soap and cleansers, our chlorine for bleaching, depend upon graphite electrodes for their very existence. Practically no other material is suitable.

Crucibles made of graphite and clay have been used since the reign of Queen Elizabeth for the melting of non-ferrous metals and alloys. Today they are indispensable in many industries. The foundry man uses graphite "facing" when he wants smooth sand cast products. The electrotyper finds it necessary in making reproductions and the painter employs it when he wants excellent protection from corrosion. Stove and shoe polishes made of graphite and carbon products allow us to touch up needed surfaces, adding gloss to our "dressing up."

When we scribble with our lead pencils, — there is no dog in dog biscuit, nor lead in lead pencils: the lead is graphite, — we make marks of carbon on our paper for some one to read.

In still another guise, we find carbon as lampblack which has been used for printer's ink ever since the invention of the printing press and until 1864 was used almost exclusively. After the advent of carbon black in 1864, lampblack was less used because of the advent of this member of the family. Lampblack is used in the manufacture of electrical machinery brushes, lead pencils, paints, inks, metal and stove polishes, phonograph records, carbon paper, crayons and as a filler for black colored materials. The early printer, laboriously producing a few impressions of his book or newspaper on a hand press, could collect enough soot for his ink by holding a saucer over a flame of a tallow candle. But the vast expansion of the printing and publishing business which has taken place in our age has brought new requirements as to ink as regards quantity, cost and quality. The inconceivably rapid operations of the modern multiple rotary press require an ink that will flow freely from the fountain, cover every hair line of the type or half-tone cut

and make an instantaneous jet black impression. For such an ink, carbon black is the ideal and indispensable material. Thus carbon enters into our books, newspapers and visual means of communication through the medium of printing inks; this printed page is a mass of markings produced by finely divided carbon black in an oil vehicle. When it is remembered that some of our daily newspapers are capable of printing two hundred and fifty thousand pages per hour, or fifty per second, all of which is done with carbon black, it can be seen that it would be impossible to continue the supply of ink requisite for printing the newspapers of the United States without it.

Carbon black is not merely the indispensable adjunct to the printing press. It is also a usual ingredient in typewriter ribbons, carbon papers and phonograph records. Thus it is a medium for the perpetuation of the typewritten as well as the spoken word.

The most remarkable chapter in the story of carbon black has been its world-wide adoption by the rubber trade during the past decade. In the early days of the bicycle and the automobile, punctures and blowouts were of frequent occurrence. Finally the rubber chemists, after a long search for something that would make tires tougher and more serviceable, hit on carbon black. Beginning with one or two American manufacturers, the use of carbon black in tire tread stocks has spread rapidly throughout the entire rubber industry of the world. Now virtually all tire treads are black. In rubber compositions in which resistance to wear is a prime requisite, such as hose, surgical and mechanical rubber, floor compositions, carbon black is an essential ingredient. A recent development is a rubber device now used instead of a shackle bolt upon automobiles to take up vibrations, remove squeaks and make riding more pleasurable.

Along with its cousins, the pigment blacks and lampblack, carbon black enters our varnishes, enamels, lacquers and paints. Carbon thus helps us maintain some of the froth of life through its use in the decorative parts of our existence.

In the form of bone black and decolorizing chars, carbon acts as a purifying and decolorizing agent in the manufacture of many materials the civilized world consumes as foods; snow white sugar is made snow white through the guiding nature of bone char and carbon used as a decolorizing char in sugar refining. Our salad oils are made more brilliant by bleaching with decolorizing carbon. Many of our pharmaceutical chemicals and drugs are purified by its use.

As metal adsorbent chars, carbon recovers gold and silver for us from metallurgical solutions. In medicine it aids us in the fight against tetanus, cholera and other diseases by adsorbing the germs and destroying them. After aiding us immensely in living our lives and making our existence a fuller, calmer and richer one, carbon saves lives in the adsorption and elimination of toxic gases against which no chemical protection exists, by the action of adsorbent and activated carbonaceous material. Its value in times of war, as protection in gas masks against lethal gases sent out on the wind by the enemy, cannot be estimated. In peace times, gas adsorbent charcoal is finding increasing application in the abatement of stenches by its adsorption of the odoriferous materials; in the recovery of valuable vapors of volatile liquids; the extraction of gasoline from natural gas; and the purification of fermentation gases such as carbon dioxide so that they might be employed in the best grades of carbonated beverages.

The essential rôle of carbon in the form of electrodes can be readily seen by its absolute necessity for our electric furnaces, where it serves to introduce current; and in the industries producing the following products:—electric steel, ferro alloys of all sorts—we live in an “alloy age” and one of stainless steel,—calcium carbide and acetylene; silicon carbide and alundum, the abrasives which make high speed manufacturing of products possible; aluminum and magnesium metals of vastly increasing application and use; phosphorus and phosphoric acid; electrical resistance wire,

upon which we depend in our toasters, percolators, electric irons and hair curlers; carbon disulphide, used in vast quantities for making rayon or artificial silk; tungsten, of our incandescent lamps; fixed nitrogen from the air as cyanamide for fertilizers and cyanides for metallurgical work and insecticides; sodium and calcium; caustic soda, chlorine and bleach, and all the electric furnace alloys of unusual compositions. The electrode today is therefore an essential part of our existence.

Carbon in arc light carbons enables us to obtain searchlights of millions of candle power. As battery carbon in dry cells, so essential to our enjoyment of radio, it is indispensable.

Carbon helps to keep the world moving, through its employment in electrical machinery brushes, carbon contacts, and battery carbons. When most other things fuse, carbon alone remains unmelted by the intense heat. It thus finds employment as resistors and refractories in certain specialized applications.

Carbon allows us to talk with each other over long distances, if necessary, for the transmitter of the telephone consists essentially of two thin disks, with the space between them filled with granular carbon. Sound waves cause variations in the pressure between the granules, which produce corresponding variations in the electric current flowing through them; the variations of the current produce corresponding sounds at the receiving end of the line.

The various forms of industrial carbon, such as diamonds, both gem and industrial; graphite, natural and artificial, in its employment in crucibles, electrodes, paints, facings, refractories and other uses; adsorbent chars of the gas, decolorizing, metal adsorbent and pharmaceutical types; bone char; charcoal as a fuel; carbon pigments such as lampblack, carbon black and the host of miscellaneous black paint and ink pigments, all of special characteristics and diverse applications; carbon electrodes; electrical machinery brushes, specialties; arc light carbons; lead pencils; resistor carbon;

contacts; carburizers; refractories; catalytic carbon; telephone disks and telephone granular carbon and the extensive field of application of carbon in industry will be discussed.

Carbon will assume greater and greater industrial importance in the future because it serves so many industries which are growing at very rapid rates. Elemental carbon started to become technically important only twenty years ago, but during the decade that has passed its related industries have grown hundreds, in some cases thousands, of times in size and in value of products produced. Carbon industries are a fruitful source for industrial research not only because of the low yields of some branches but on account of the fact that so very little work has been done in proportion to the amount of improvement possible and very probable.

CHAPTER II

DIAMONDS

THE diamond is the hardest and most imperishable of minerals. It has ranked as leader among precious stones for centuries, and in early times was credited with supernatural qualities, such as the power of averting insanity and neutralizing poisons. The ancient pharmacopoeias contained many remedies compounded with this mineral. In the Middle Ages the diamond was known as the peacemaker between husband and wife, which attribute still holds good. The diamond derives its name from the Greek word "adamas" meaning invincible.

The *hardness* of the diamond makes it indispensable for many abrasive purposes. Numberless efforts have been made to produce diamonds artificially, but thus far without commercial success.

Physically, the diamond has been the subject of much study. Its base, carbon, is chemically identical with graphite or charcoal, into which it can be resolved by the action of heat or electricity.

The diamond is always found in single crystals which show no signs of having been previously attached to any matrix.

The diamond ordinarily is found crystallized in the isometric system, as tetrahedral forms. They are usually octahedral in habit but the faces are commonly curved or pitted as Fig. 1. Curved faces of the hexoctahedron are frequently observed, as Fig. 2. Twins (Fig. 3), with the octahedron as the twinning plane, often flattened, sometimes occur. Crystals with cubic and dodecahedral planes are rare. Commonly the crystals are distorted into elongated or irregular forms.

Diamonds show, except in those forms which are spherical with radiating structure, perfect cleavage parallel to the octahedral faces. The crystals are usually transparent but they may be translucent or opaque.

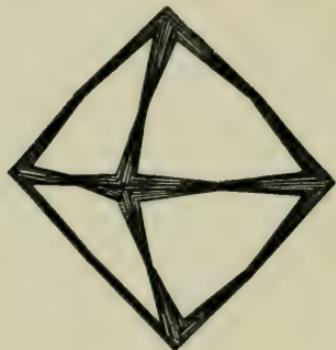


FIG. 1.—DIAMOND CRYSTALS.
PITTED FACE OCTAHEDRON

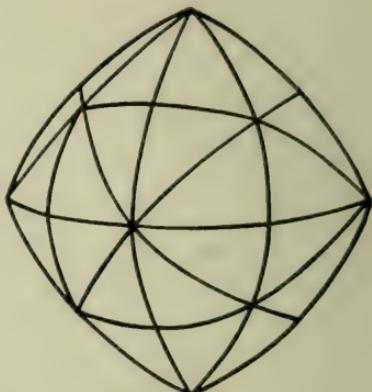


FIG. 2.—CURVED FACE HEXOCTAHEDRON

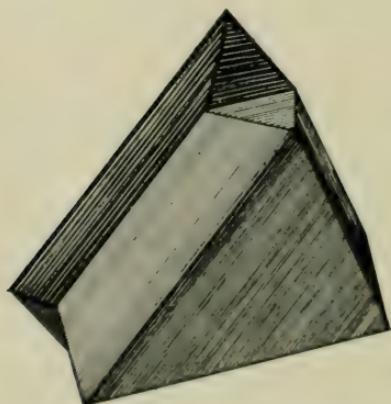


FIG. 3.—DIAMOND CRYSTALS.
TWINNED OCTAHEDRON

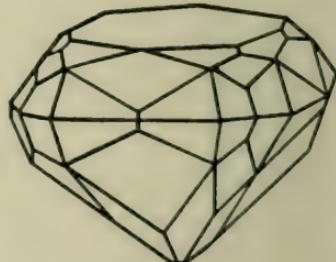


FIG. 4.—“BRILLIANT” CUT GEM

The use of the diamond as a gem dates back prior to 400 B.C. when it was used ornamentally by the Greeks, Phoenicians, and other races. Diamonds are sparsely dis-

tributed in different parts of the world. The earliest ones found were alluvial, occurring like gold in the beds of streams and rivers.

The diamonds which are not alluvial are found in a heterogeneous mixture of fragments of various rocks and minerals cemented together with a bluish green indurated clay known as "blue earth." The diamond-bearing earth is a volcanic plug, consisting of the breccia of several rocks chiefly peridotite. The diamonds are found imbedded in the blue earth.

The mines in India are the oldest workings; they have yielded some of the finest and most prized stones. Many of the famous old fields are now abandoned but work is still carried on by natives in the district south of Allahabad and Benares. At present the yield is small. There are mines in Borneo. The states of Bahia and Minas Geraes in Brazil (at Diamantina, Bagagem, Grao Mogul) have been famous for their diamond mines. Diamonds have been found in small quantities in British Guiana, Colombia, Mexico and in a number of states of the United States, notably Arkansas. Diamonds were discovered in the Urals about 1829 and in Australia in 1852. The discovery of diamonds in South Africa dates back to 1867. Operations in this field were more prolific as the diamond-bearing pipes were promptly located, and such mines as the De Beers, Kimberly, Jagersfontein, and the Premier opened. The fields of South Africa (Jagersfontein, Koffyfontein, Kimberly, etc.) have been the most prolific source in recent years. The South African mines, it is estimated, are responsible for over 96% of the world's diamond production.

The fact that diamonds are found in one place is no guarantee that they exist nearby. In South Africa diamonds are mined in "pipes" of blue clay, apparently of volcanic origin, which usually extend vertically for thousands of feet but cover only a small area horizontally. The principal mines in South Africa are equipped with modern machinery so that hand labor is almost entirely eliminated.



FIG. 5.—THE PREMIER DIAMOND MINE IN THE PRETORIA DISTRICT
OF THE TRANSVAAL, SOUTH AFRICA
(Courtesy Engineering & Mining Journal)

Fig. 5 shows a view of the famous Premier Mine in the Transvaal, South Africa.

The volcanic "pipe" mines are now the most important diamond sources. The blue earth is mined, brought to the surface and allowed to weather. In about a year it disintegrates and becomes friable. It is then crushed and washed to separate the clay into earth and gravel. The diamondiferous gravel is then graded on screens. Each grade drops to a pulsator table where it is sorted into materials of different specific gravity. The higher portion is washed to the end of the trough and disposed of as tailings. The diamond yield per ton of blue earth mined and treated is approximately one half carat. The heavier portions fall through a grate and are conveyed to grease-smeared shaking tables. The diamonds adhere to the grease, the other

constituents flowing on over the end of the tables to the tailings dump. Sometimes the tailings are conveyed to a second table and the reject of this examined and any diamonds picked out. The stones adhering to the table surfaces are scraped off with the grease and separated from the grease by melting it off. The grease is then returned for re-use. The diamonds are examined on a sorting table, picked over and separated from heavy mineral associates such as pyrites, barytes, etc., by hand.

Diamonds were first discovered in Brazil in 1725, at which time two Jesuit missionaries, while passing through certain parts of Minas Geraes on the way to the Rio Sao Francisco, found the natives playing a peculiar local game in which small shiny pebbles of various colors were being used as counters. These missionaries traded a few trinkets for a quantity of stones, which they took back with them to civilization. As soon as the value of the stones became known, the Portuguese government sent out fiscals who systematically started working the diamond fields with slave labor. The work continued for years, during which time many thousands of carats of diamonds were recovered. A strange coincidence in connection with the Brazilian diamond fields is that until quite recently no pipe or "mother lode" was discovered — all stones found were taken from the rivers. While these deposits do not conclusively prove the existence of "pipes," it is generally conceded that the soft white soapy "*massa*" which carries the diamond is decomposed kimberlite, and that the true olivine, in its original state, will be found when this decomposed over-burden will have been removed. Fig. 6 shows the type of country where Brazilian diamonds are found.

In many sections of Brazil and British Guiana, diamonds exist chiefly in alluvial deposits, whence they are recovered by the natives who employ primitive hand-panning methods. A visit to a diamond mine is usually disappointing. There is little romance or excitement, as the recovery of one carat of diamond often involves the digging and washing of many

INDUSTRIAL CARBON

tons of rock and soil. The finding of a large stone arouses some interest, but is considered part of the routine work.

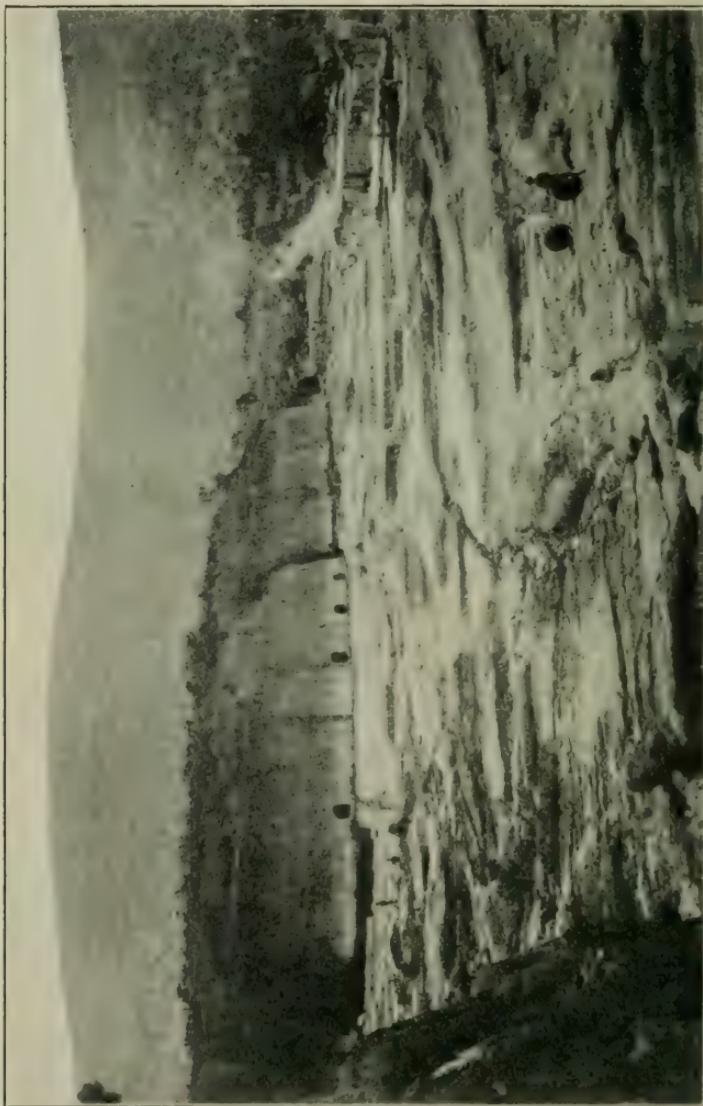


FIG. 6.—WHERE BRAZILIAN DIAMONDS ARE FOUND
(Courtesy Diamond Drill Carbon Co.)

In fact, so accustomed have the miners become to handling diamonds that they regard them almost with indifference unless an exceptional stone should flash.

Diamond stones in their natural state over an ounce in size are comparatively rare. There are, however, many historical and celebrated diamonds, the largest of which is the Cullinan, weighing $3,025 \frac{3}{4}$ carats, over $1 \frac{1}{4}$ pounds. Diamonds in their natural state are more or less rounded. Their lustre is adamantine. The lustre and sparkle of the gem diamond only appears after cutting and polishing. The diamond-cutting industry was largely developed in Amsterdam and Antwerp. The shape of the so-called crystal as it leaves the diamond cutter has no relation to the natural crystalline shape. The loss in cutting amounts to one half or more of the diamond. It is stated by competent authorities that in cutting the "brilliant" (Fig. 4) only 42% of the original weight of the stone remains in the finished cut gem. In the rose cut, the loss due to cutting is somewhat less. The lapidary desires to obtain the maximum reflection from the interior of the stone. The standard gem shapes are the rose and brilliant. The latter has a rather large flat face which is really the base of a pyramid with many sides called "facets." The high reflecting and refracting power of the cut stone is the particular quality which makes it supreme among gems. The light falling on the front face of a brilliant passes into the gem and is reflected from the interior surfaces of the facets. The reflected light is refracted into a wonderful prismatic display.

INDUSTRIAL DIAMONDS

The earliest recorded industrial use of diamonds antedates 1000 A.D., at which time diamonds for cutting were used in the East. There are three well defined varieties of diamonds, all of which are used industrially. First, the crystallized or gem variety; second, bort, also known as "bortz," "boort," "boart," and "bowr," a round form with radiate or confused crystalline structure; and, third, carbonado, also known as black diamond carbon or carbonate, an impure aggregate of small diamond crystals,

forming a rock of granular but compact texture and without cleavage. It is massive in form and opaque. The definitions of gem and carbonado are followed by the trade, but the term bort is extended to all impure diamonds and even to fragments and powder of gem diamonds which are valueless as gems because of impurities or their small size. A special variety of bort, round in form and light in color, consisting of crystals radiating from a common center is known as "ballas." It is relatively rare and its use is advised as a

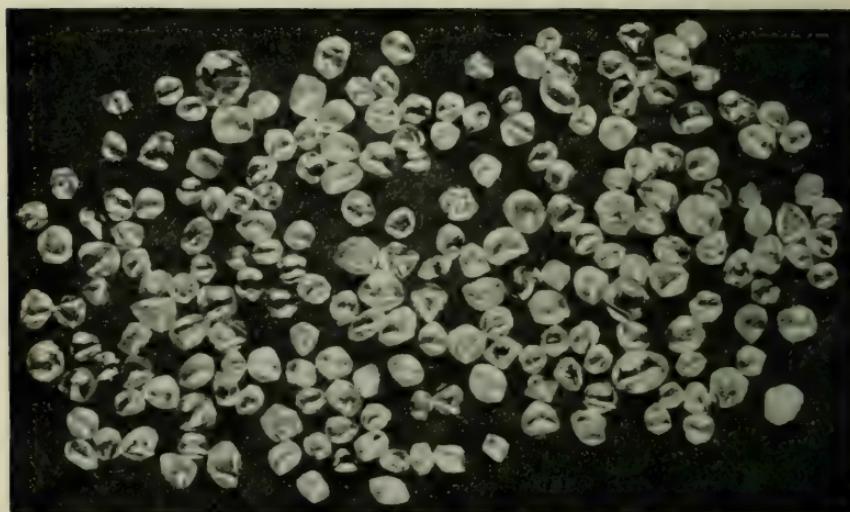


FIG. 7.—NATIVE BRAZILIAN DIAMONDS
(Courtesy Diamond Drill Carbon Co.)

test stone for determining the hardness of diamonds. It is stated that only a dozen or so of the bigger sizes of ballas are found on the average every month. Carbonado in important quantities is found only in the states of Bahia, and Minas Geraes, Brazil. The Bahia carbonado occurring in stream gravels in association with gem diamonds was first found in 1843, although up to 1856 it was thrown aside as waste. The production of carbonado in Bahia is estimated at 20,000 to 30,000 carats annually.

Carbonado in the early days of the industry was sent to

Amsterdam in ordinary kegs owing to its low value. In 1843 it was worth only a cent a carat, which price rose in 1872 to approximately fifty cents a carat. It was then used as diamond powder. At the present day, its value is considerably in excess of \$100 (now approximately \$150) a carat for good two to three carat stones. The retail price of carbonado is given in Fig. 8. Fluctuations in prices of

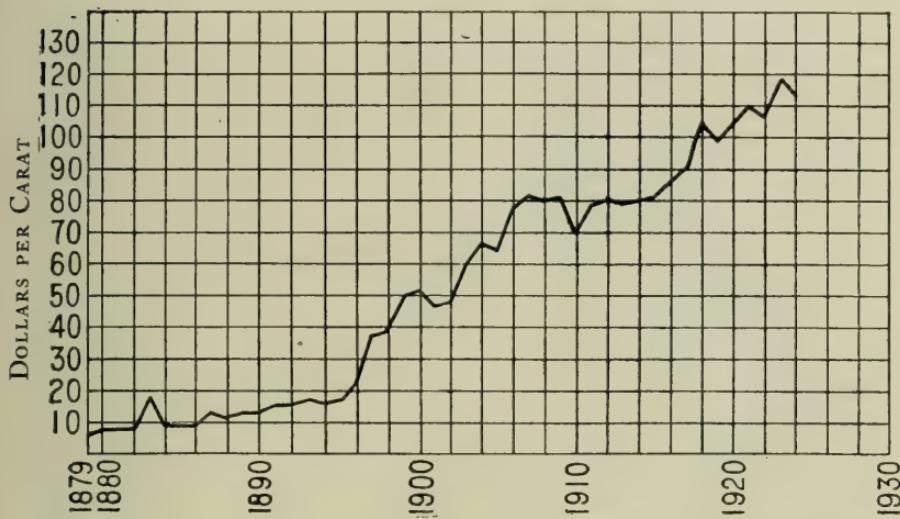


FIG. 8.—GRAPH OF RETAIL PRICE OF CARBONADO PER CARAT. GOOD 2 TO 3 CARAT STONES

gem diamonds and industrial diamonds are independent of one another. The value of carbonado is dependent upon the size of the stone and its quality, the value per carat of a one-half carat stone being about one half of the carat stone and about one third of that of a three carat stone. No new carbonado areas are being found. The price of the material should increase as the demand is increasing.

Carbonado is opaque. It is found in various colors,—black, dark green, brown, red and gray. Most stones, however, have a dark, lustrous black surface. They range in size from a quarter of a carat to several hundred carats each. Large stones must be split by pressure into market-

able shapes and sizes. Carbonado splitting usually requires expert skill.

A large carbonado is shown in Fig. 9.

The inner faces of freshly broken carbonado show light gray in color and resemble close-grained steel. The broken



FIG. 9.—1 CARBON—922.10 CARATS. NATURAL SIZE
(Courtesy Van Itallie Co.)

surface gradually oxidizes when exposed and finally assumes a dark ash gray color. Carbonado, being a confused aggregate of very small crystals, has no planes of cleavage and is therefore less liable to fracture. Greenish black stones that show surfaces like fractured steel when split,

greenish and reddish stones which show very small crystals, are stated to be the best. The reddish coloration is due to iron oxides. The diamond merchants carry several qualities which are variations in hardness, abrasive nature and resistance to fracture.

The mining of carbonado in Brazil is very crude. It is stated that a total of 300 square miles is worked. The total production has been large, despite the fact that, in comparison to metalliferous mining, only relatively small areas have been exploited.

The black diamonds are found in the old river beds. The miners try to find a place where the bedrock is high and the values concentrated, so as to have less trouble with seepage water. They then remove the overburden, which consists of clay, mud, and sand about fifteen feet deep. After the removal is completed, they have reached the diamond-bearing gravel, which ranges in thickness from 1 to 6 feet. They remove the gravel manually. The gravel is piled up near the river.

At the gravel pile the largest stones are picked out by hand. The remainder is taken to the river, where washers await it. They have erected a tripod over the water, from which a fine mesh screen is suspended by a rope, which allows the screen to sink a little way into the water. After loading it they move the screen forward and backward until they have separated out all the sand. The gravel remaining is then placed in another screen which has a large mesh. Under this they put a batea, a large wooden concave bowl, submerged in the water. This screen is then agitated, the finer material falling into the batea. The coarser material which remains on the screen is sorted for carbonado and diamonds. Material in the batea is then successively screened through smaller mesh screens, the larger stones being sorted by hand in each case. The final product is too fine to be successfully sorted by hand. The gravel is concentrated by whirling in a batea which rests on the water.

In a number of mines, screens woven of metal wires are

not available. Fixed washing screens, made in steps, are then built up of thin twigs of trees and bushes. This method is very crude and primitive.

The sizes of carbonado range from $1/16$ carat (about the size of a small pinhead) up to several hundred carats each. A carbonado was found in Bahia that weighed 3,078 carats. At present market price it would have been worth over \$300,000.

Bort occurs in the Brazilian and British Guiana alluvial



FIG. 10.—SCREENING AND WASHING DIAMOND BEARING GRAVEL
(Courtesy Engineering & Mining Journal)

deposits and in the South Africa pipe and alluvial mines. The best grades are the Brazilian ballas, equal in value to the better grade of carbonado. Yearly production is probably only a few hundred carats. These stones are usually globular. They are very hard. Bort is distinguished by the diamond merchants as Cape Round borts, Cape ballas, Brazilian bort, and qualities known by the name of the mines producing them. Many of these borts are impure white, brown, black or yellow diamonds that have less value for polishing than for industrial purposes. Bort prices vary

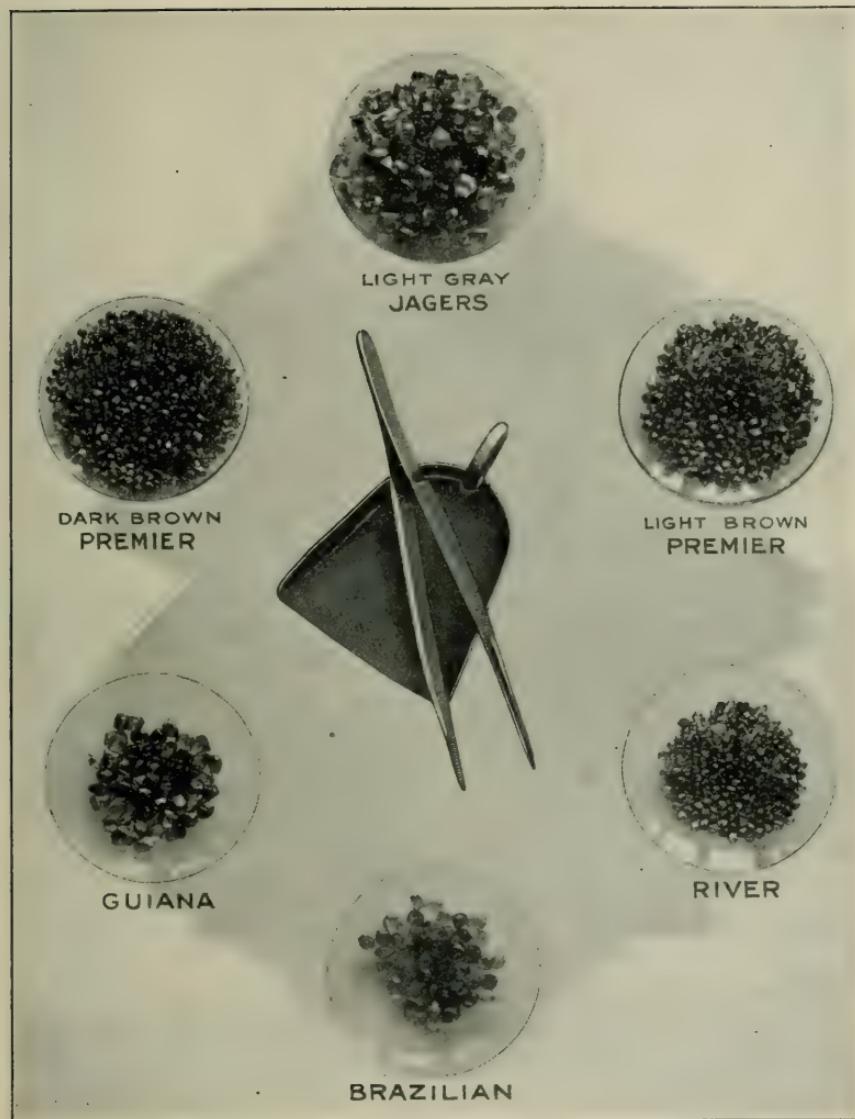


FIG. 11.—BORTZ FROM THE WORLD'S PRINCIPAL DIAMOND FIELDS
(Courtesy Diamond Drill Carbon Co.)

according to the grade and the size of the stone. Its value at the present time is from \$10 in the poorer grades to \$35 a carat in the best grades. These prices are one fifth to one

fourth the price of the corresponding sizes and grades of carbonado. The rejections from gem mining are also known as bort. About one half of the South African pipe mine production is suitable only for industrial purposes, the alluvial mines producing relatively less poor material. Exclusive of crushing bort, the world's annual production of bort (from mines) is from 35% to 40% of the total diamond production in the shape of uncut stones. The dust and small fragments resulting from cutting gem material increase the bort production to more than one half of the total diamond production of the world. The world's production of bort is somewhere in the neighborhood of 2,000,000 carats a year. Brazil probably produces 25,000 carats of carbonado annually.

America, owing to her highly developed industries with large scale and rapid manufacturing, is probably now or shortly will be the largest consumer of industrial diamonds. They are used for lathe tools, as diamond dust, as dies for wire drawing, drills and glass cutting tools.

Diamonds are cut into various shapes and set in lathe tools employed for a large number of purposes. The tool allows increased speed with small tool wear. Their satisfactory performance causes them to replace alloy steel tools more and more. Carbonado is most suited for this purpose as it is less likely to fracture and is more readily shaped. Bort, on the other hand, because of its relative cheapness, finds its largest use in this field. A constantly increasing use of diamond set tools is in truing abrasive wheels. They are also used to shape wheels for grinding special parts. 85% of the stones used for this purpose are bort with a small proportion of ballas, the rest being carbonado. The use is particularly large in automotive factories, where the position of the diamond setter is now well established. Diamond set tools are used for cutting hard substances such as hard rubber, ivory, electric light carbons, vulcanite, etc. They are also used to shape felt rolls in paper mills. Where the steel tool scarcely makes an impression on this hard fibrous

substance, the diamond quickly gives the roll a smooth finish like that of polished wood. Diamond set tools are used for finishing very accurate machine work, single motor factories alone using industrial diamonds to the value of \$150,000 annually.

Diamond dust is a superior abrasive due to the rapidity with which it does its work. As its grain size is not rapidly reduced it does even, dependable work, superior to that of carborundum or other cheap abrasives. Carbonado is preferred by the optical trade which is willing to pay up to \$5 a carat for it. What is probably the largest use of diamond dust is its employment in polishing diamonds and gem stones. It is used on both the diamond cutting and lapping wheel. It is also used on saws, either by beating into the edge of non-ferrous metal disks, or feeding to the saw cutting surface in oil. The metal most commonly used is phosphor bronze. Optical glass as well as alloy steels are split with such saws. Holes are drilled in precious stones by spinning a copper or iron tube or drill, fed with diamond dust and oil. The hole is usually started with a diamond splinter.

Dies for wire drawing constitute one of the principal uses for industrial diamonds. They were first commercially used about 1868. The stones used are cleavage plates or thin crystals and ballas, weighing from one half a carat to ten carats. A hole, tapered at either end, is started in a thin fragment of diamond by a diamond point and finished by a steel drill fed with diamond dust. The process is long and tedious. The stone makes up 40% to 60% of the cost of the die, labor 30% to 32%, and the diamond dust used in drilling 22% to 30%. The drilled diamond plate is then mounted in a non-ferrous metal disk. When the aperture of a die has enlarged through use, it is redrilled to draw the next largest size of wire. Two years constitutes the average life in service. Wire of uniform size and high polish, even when of very fine gauge, is produced. The sizes vary in diameter from 0.114" (2.9 mm.) to 0.0008" (0.02 mm.), although holes as small as 0.0004" (0.01 mm.)

have been used. When fine wire is drawn successively small dies are used, the usual practice employing diamond dies only in the final drawing. Coarser work uses much cheaper hard stones or alloy steel dies. Tantalum, tungsten, and osmium filament for electric lamps are drawn through diamond dies. Named in the order in which they wear the diamond dies, copper, gold, silver, brass, bronze, iron, platinum, monel metal, nickel, and crucible steel wires are also drawn through the diamond dies. In the case of the latter hard metal the diamond consumed is higher. The life of a diamond die can be judged when factories draw 300 to 400 tons of copper wire through a single die without variation in gauge.

Diamond drilling is one of the most important uses of carbonado. Some diamond dealers estimate that in boom mining times, 7,500 to 10,000 carats are used annually. Others place the figure at 15,000 carats. The process was invented in 1863. Carbonado is by far the most satisfactory for this purpose. The cheaper ballas or bort are applicable only in soft formations. The carbonado to be used in diamond drilling is broken up into fragments weighing usually up to three carats, or in instances as much as twenty carats. The stones are mounted in metallic drilled heads. All beating is avoided in mounting stones and in drilling so as not to expose them to shocks, for, although the diamond can bear a very high pressure, it is not able to resist blows. The diamond merchants advise stones of cubical, spherical, or oblong shapes for diamond drilling. As much as \$25,000 worth of carbonado has been used in drilling single holes.

Diamonds, frequently of gem quality, varying in size from one eightieth of a carat to one fourth of a carat, are largely used in glass cutting. There are about thirty stones to the carat. The majority of glaziers' diamonds formerly came from Brazil, but now most of them originate in the South African mines. Good stones are scarce and the price is approximately \$40 a carat. The diamond is set in a fusible metal at the end of the handle. The stones are re-

set in the tool when the edges are dulled. Angular diamond crystals produce satisfactory cuts on glass so that it breaks along the groove so produced. The cutting edge is formed by markedly curved faces cutting at not too obtuse an angle. The edges and ends of rolled plate glass, after it comes from the annealing kiln, are trimmed with diamonds.

Diamond points set in drills are widely used in boring holes in watch jewels, optical instruments, and drilling very hard substances with extreme accuracy of gauge. They are also used for making etching marks or engraving on scientific equipment and in making intaglios. A number of phonograph manufacturers produce diamond pointed reproducing mechanisms. The use of diamond dust for cutting and polishing plating stones has been largely supplanted by carborundum, alundum, and other synthetic abrasives.

CHAPTER III

NATURAL GRAPHITE

HISTORY. Graphite (Γροφειη, Greek "to write") was known in early times for it has been found, as a result of its use for decorative purposes, in prehistoric burial places in Europe and in ancient graves.

It first came into general use many centuries later. The earliest mention is found in the Middle Ages as a substance for use in drawing. Its true nature and identity were not recognized until the end of the 18th century, when Scheele (1742-1786) demonstrated its carbon content by igniting it in a current of oxygen. The name graphite was first given to the mineral by the mineralogist Werner in 1789.

Graphite differs to a remarkable degree from the diamond and amorphous carbon (charcoal) in its outward characteristics, such as form, color, hardness, as well as in many of its properties. The three forms can be readily distinguished by chemical and physical tests. The specific gravity of charcoal is 1.3 to 1.9, graphite 2.1 to 2.3, and diamond 3.5. Chemically a ready means of differentiating between the three forms is to treat one part of the substance to be tested with three parts of potassium chlorate and sufficient concentrated nitric acid to render the mass liquid, the mixture being heated on a water bath for several days. The diamond is entirely unaffected. Graphite is converted into golden yellow flakes of graphitic acid. Amorphous carbon is altered to a brown substance soluble in water. Many so-called graphites, when tested in this manner, are shown to be charcoal, natural coke, carbonaceous shale, or even coal. Coal or carbonaceous shale may be detected by the

presence of considerable volatile matter. All of the adulterants are conspicuous by reason of their low ignition temperatures, as compared with graphite. Coke and retort carbon react actively when fused with sodium sulphite, while graphite does not reduce this salt.

Graphite is a black, lustrous mineral crystallizing in the hexagonal system, with rhombohedral symmetry. The crystals have tabular form, are six sided, and the faces are commonly striated. They are seldom very distinct because of the softness of the material. Graphite is softer than talc, which is 1 on the Von Moh hardness scale, of which the diamond is 10. Very perfect graphite crystals are found in the crystalline limestone of Pargas, in Finland, but the best specimens have been obtained from meteorites. Crystals in parallel intergrowth, or twins, have been reported.

The streak of graphite is black and lustrous. The mineral is easily sectile, flexible but not elastic. Owing to its softness it marks other substances readily and is greasy to the touch. It is a good conductor of heat and electricity. The flakes have a perfect basal cleavage and are opaque even in the thinnest scales. Graphite is very resistant to weathering influences. Perfectly bright flakes are commonly found in the surface soil formed by the disintegration of graphite bearing rocks.

Graphite is highly resistant to attack by most chemical reagents. Fusion with alkaline carbonates produces carbon monoxide, which puffs through the molten material and ignites as fast as it is formed. The graphite is consumed in reducing the carbonate. Molten alkalies, at low red heat, do not appreciably attack graphite but separate it from mineral associates by their action on them. Pure graphite is not affected by dry chlorine gas, hydrochloric or hydrofluoric acids. Graphite may be completely oxidized by a mixture of chromic and sulphuric acids. Graphite is resistant to the action of most acids, bases and salts.

The natural graphites are divided into three classes, according to the character of the mineral. These three divi-

sions comprise disseminated flake, crystalline or plumbago, and "amorphous" or black lead.

Flake graphite is a scaly or lamellar form commonly found in metamorphic rocks, such as crystalline limestones, gneisses and schists. In such cases, each flake is a separate individual and has crystallized as such in the rock. Plumbago is the mineral as found either in the form of more or less well defined veins or as pockety accumulations along the intrusive contacts of pegmatites (usually) with limestones and schists. Both types of occurrence are fundamentally similar in that they represent fissure or fracture filling by graphite, the shape only of the ore body being different and the amount of foreign mineral substance in the form of crystallized, contact metamorphic minerals being greater in the latter case than in the former. Plumbago or vein graphite deposits are of two types, foliated or bladed, and columnar or fibrous. The terms, plumbago and black lead, still used by the trade, date back to the time before Scheele proved graphite to be carbon, dispelling the old idea that the graphites all contained lead.

Amorphous graphite is commonly found in the form of minute particles more or less uniformly distributed in feebly metamorphic rocks, such as slates or shales; or in beds consisting practically entirely of graphite. The latter usually represent metamorphosed coal seams, and carry as high as 80-85% graphitic carbon, while the former, being altered carbonaceous sediments, commonly range from 25 to 60%. The graphite content of such amorphous deposits is dependent on the amount of carbon originally present in the sediments. There is no evidence of any enrichment being caused by the intrusive rocks that have been the metamorphosing agencies in some cases. Certain amorphous graphite deposits have undoubtedly been formed by the agency of igneous intrusives, while others are probably the result of dynamic metamorphism.

Space does not permit a discussion of the theories of the geological formation of graphite. For such the reader is

referred to the works of Cirkel,¹ Donath,² Haenig,³ and Spence.⁴

Oxidation of certain amorphous graphites, such as the Bohemian, for instance, produces a yellow powder graphitic acid. Ceylon plumbago yields a lamellar crystalline graphitic acid. On decomposing by heat, the powdery graphitic acid gives a product resembling lampblack, while the crystalline acid decomposition result is lighter in color and does not appear to be in as fine a state of subdivision. These results might indicate that there may be structural differences in the forms of these types of graphite. The subject has not been sufficiently investigated to warrant any conclusions.

Other graphites, when moistened with fuming nitric acid and then heated, swell up, assuming vermiform shape, have a circumference of $\frac{1}{4}$ " to $\frac{1}{2}$ " and a length sometimes of several inches. The volume of these "worms" is often a hundred or more times that of the original graphite. The color is steel gray with a metallic lustre. The forms are bent and twisted in regular curves. It is thought that the cause of the phenomena is the capillary structure of the flakes, which permits them to absorb the acid readily. On heating, the gases generated exfoliate the graphite.

When finely powdered graphite is heated with a mixture of one part of nitric acid and four parts of strong sulphuric acid, it assumes a purple tint. The same effect is produced upon heating a mixture of 14 parts graphite, 1 potassium chlorate and 78 parts strong sulphuric acid. Washing the material restores it to its original color. It is no longer graphite, but contains oxygen, hydrogen and sulphuric acid. When this is heated to redness, it swells up with a copious gas evolution and then falls to an extremely fine powder of pure graphite of a specific gravity of 2.25 (so called "Brodie's graphite").

¹ Cirkel, Report No. 18, Graphite (1907) Canadian Mines Branch.

² Donath, *Der Graphit*, Leipzig (1904).

³ Haenig, *Der Graphit*, Wien (1910).

⁴ Spence, Report No. 511, Graphite (1920) Canadian Mines Branch.

Acid treatments have been employed for the purification of natural graphite.

Artificial graphite does not possess the property of swell-

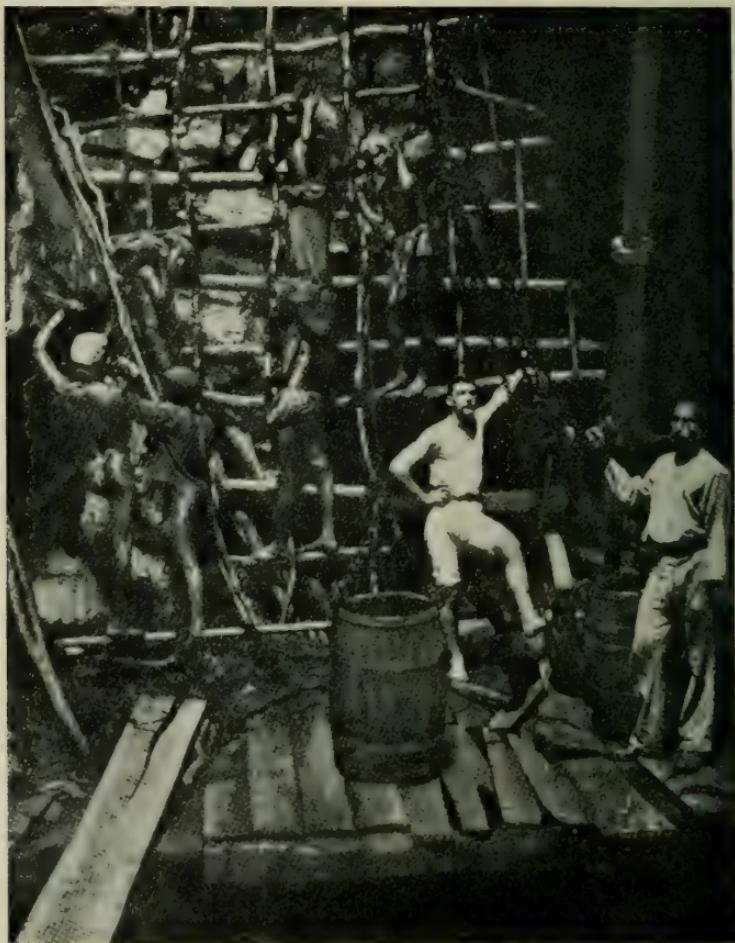


FIG. 12.—IN A CEYLON GRAPHITE MINE
(Courtesy Jonathan Bartley Crucible Co.)

ing up when treated with nitric acid. Graphites separating out of fluid metals possess it very markedly.

The crystalline graphites or plumbago are the purest of the natural graphites. As a result of their vein occurrence,

the amount of mineral impurities, which are generally calcite and quartz, is small. The crude ore runs 60 to 70% graphite. At the Ceylon mines, which produce practically all the world's supply of plumbago, the ore is first roughly picked over, the attached gangue reduced to 5 to 10%, and then shipped to the curing or dressing compounds on the coast. Here the larger pieces are picked out and the remainder sized by means of stationary inclined screens. The large pieces are broken up by hatchets, and the impurities removed as far as possible by picking. The cleaned graphite is similarly sized. The larger pieces are placed on pieces of wet sacking, again picked over, rubbed up by hand and polished on a fine mesh screen placed flat on the ground. These larger sizes, which measure up to 1" across, are graded as "ordinary lump" and "medium lump." They command the highest prices. The graphite which passes through the screens is graded into "chip" and "dust" according to its size.

The lower grade material is pulverized with wooden mauls or beaters, placed on sacking and sorted by hand. In some cases, cleaning is effected by washing in saucer-shaped baskets, moved by hand with a panning motion through water. The graphite is thrown off into the water, the particles of gangue remaining in the basket. The cleaned graphite is shovelled up and dried by sun heat on drying floors. The dried graphite is winnowed into "dust" and "flying dust."

Considerable attention is paid to the blending of Ceylon graphite which is the mixing of the product of various mines. The main grades, lump, chip and dust, are further classified into several quality subdivisions.

A procedure as this is only practicable in countries where cheap labor is obtainable. In the treatment of plumbago mined in North America, the usual method of ore dressing has been to break it up by hand into medium sized pieces, cobbing out the gangue and discarding the waste. When a mill is available, the material is run through mechanically.

Modern labor saving machinery has been introduced into Ceylon several times, but each time the equipment has been broken and destroyed by native labor which feared displacement by power driven apparatus.

Practically all natural graphites contain admixed mineral impurities, the proportion of such impurities being greatest in the flake ores. Many of these are really crystalline



FIG. 13.—PANNING GRAPHITE IN A CEYLON COMPOUND

(Courtesy Jonathan Bartley Crucible Co.)

schists, in which the graphite has been developed subsequent to the formation of the rock proper. The usual impurities are mica, calcite, quartz, feldspar, pyrites and pyrrhotite, and various calcium, magnesium and aluminum silicates. Where pronounced weathering of such ores has occurred, many of the above minerals are not to be recognized in their original form, having been converted into

clayey material. A considerable enrichment of graphite may have resulted. Fresh unaltered flake ores, examples of which are many Canadian deposits, range from 10 to 30% graphite. Soft decomposed ore, such as the Passau, Bavaria, mines, run from 30 to 50% graphite.

The extraction of flake graphite from its ores and its preparation for market has always presented difficulties from both the technical and the economic side. The minerals associated with flake form 75 to 95 per cent of the ore and possess specific properties varying little from those of graphite itself. Mica is of somewhat the same form, hardness and toughness and behaves in much the same fashion as does graphite at all the stages of the mechanical treatment. It is one of the most difficult minerals to eliminate. Its low fusion point causes its presence in crucible graphite to be highly objectionable.

The crucible trade, which uses about three quarters of the world's output of graphite, demands the best quality, pays the highest prices and specifies No. 1 flake. This material must contain 90% carbon or better, and be of such a screen size that all of it passes through a 20 mesh but is retained on a 90 mesh screen. Processes have been devised which have proved more or less satisfactory as far as carbon content and size of flake is concerned. These results, however, have always been achieved at the expense of recovery, and frequently also by some system of retreatment that rendered operations unprofitable. It is probably not an overstatement to say that, by any of the concentrating systems hitherto employed on the American Continent, excepting oil flotation, the average loss of graphite in the tailings has been not less than 50% of that contained in the original ore. This has been due to the fact that it has always been found practically impossible to free all of the flake completely from the gangue without reducing an undue proportion of it to the powder form, unsalable for crucible manufacture.

Graphite ores vary so widely in their character, proportion of large size flake, nature of the associated minerals,

hardness, and graphite content that it is quite impossible to outline any mill method that will even approximately suit a majority of ores. For data on milling methods used and now in operation, the reader is referred to the treatises on graphite previously cited.

The profitable operation of a dressing plant is essentially dependent upon its production of No. 1 flake, as the market for No. 2 flake and dust is uncertain. The prices offered for the lower grades are out of all proportion to the cost of production. It is essential for a mill to recover sufficient No. 1 flake per ton of ore to meet the cost of mining and milling. In Alabama and Pennsylvania, most of the ore milled is weathered surface schist, which, though running only 3 to 5% graphite, requires little grinding to free the flake. The New York and Canadian ores are weathered only a short way down, most of the ore being hard and requiring considerable grinding.

Amorphous graphites vary so widely in their carbon content and physical character that the treatment to be undergone depends largely on the use to which the material can be put. Mexican graphite is of exceptionally high grade, being 86% carbon. For this reason and on account of its extreme softness, it is well adapted for pencils and lubricants. Rhode Island graphite is impure and somewhat hard. It is employed almost exclusively for foundry facings. Other impure, amorphous graphites, carrying 35 to 50% carbon, can be utilized in paints, stove polishes and similar purposes. This ore is generally prepared by hand picking and grinding. For many purposes a high carbon content is not essential, and the presence of a considerable proportion of clayey matter is not objectionable.

It is practically impossible to refine amorphous graphite mechanically as a result of the intimate association of graphite and mineral matter. Practically all amorphous graphite deposits are metamorphosed coal seams or metamorphosed carbonaceous shales or slates. The possible uses for the graphite are almost entirely dependent upon the variety and

character of its impurities. The product, ground fine or air floated, is used for paints, lubricating greases in some cases, stove polish, electrotyping and boiler graphite, while certain grades such as the Sonora Mexican are in special demand for pencil manufacture.

CHAPTER IV

ARTIFICIAL GRAPHITE

THE artificial graphite industry is very closely connected and interrelated with that of carbon electrodes and the electro-chemical industries.

In 1893 in a lecture before the Société International des Electriciens, Girard and Street¹ of the Société "Le Carbone" described a furnace for the conversion of carbon into graphite. The method consisted in causing a series of arcs to play over the surface of the carbon to be converted. It was stated that an 85 per cent conversion was obtained. It is not known whether this method was ever commercialized.

In 1896 H. Y. Castner² patented a process for heating carbon electrodes by means of electricity so that "a graphite-like form of carbon was produced." It might be assumed that this anticipated Acheson's graphite electrode, were it not for the fact that Castner remarks that the resulting electrode "will be found to be of decreased density." The Acheson electrode, after conversion to graphite, has a higher density than its amorphous raw material. Castner also states "that the temperature produced is such that the carbon will give off the more flammable material it contains." Accordingly his patent merely covered the electrical baking of carbon electrodes.

In 1896 E. G. Acheson, then of the Carborundum Co., was granted a patent for the manufacture of graphite in an electric furnace. He heated carbon "in association with one or more oxides to a temperature sufficiently high to cause a chemical reaction between the constituents and then con-

¹ Bull. des Société des Electriciens, vol. 12, p. 246.

² United States Patent 572,472, December, 1896.

tinued heating until the combined carbon separated out in the free state." He goes on in his patent to say: "It is not, however, limited to the use of oxides, as pure metals, their sulphides and other salts may be used; but for various reasons the oxides are to be preferred."

Three years after the patent was obtained the Acheson Graphite Co. was incorporated and started building a plant at Niagara Falls, which is now the center of the industry. The company proposed that several distinct forms of the product were to be produced. "One consists of forms or articles made out of amorphous carbon, with the desired amount of impurity added, which will afterward be heated in an electric furnace and converted more or less to graphite." Acheson had been doing this work for a year or more previous in the furnaces of the Carborundum Co. He had made about "200,000 carbon electrodes, measuring 15 in. in length, with about 1-in. cross-sectional area, for use in the Castner alkali process, nearly half of them having been shipped to Europe."³

To quote again from Acheson, writing in 1899: "It is not the present intention of the company to enter into the manufacture of their product into the finished form for the general market, but rather to encourage those now engaged in making the natural graphite into articles of commerce to become buyers of their material, substituting it for the natural product now used." He states that according to the company's plans, "they will erect machinery for reducing coke to grains of the desired size, an electric furnace through which the prepared grains will pass in a continuous stream, a pulverizer for reducing the grains as they are received from the furnace, and a scalping sieve through which the product from the pulverizer will pass, so that the particles exceeding 1/200 in. in diameter may be removed. The final flour will contain an amount of pure graphite proportional to the percentage of the original coke."

³ E. G. Acheson, "Graphite, Its Formation and Manufacture," J. Frank. Inst., 1899, pp. 475-486.

It is interesting that graphite was first shown by Scheele to be an elementary body and an allotropic form of carbon in the first year of the 19th century and in the last year was made to order in great quantities and was rapidly becoming an article of commerce.

The original discovery that graphite could be produced in the electric furnace was made as a development of Acheson's earlier discovery of the method of manufacture of carborundum. In studying the effect of very high temperatures on carborundum, it was found that the material decomposed at about 7500° F., the silicon being vaporized and the carbon being left behind not in an amorphous but in a graphitic form. Eventually a method was developed for making graphite from anthracite coal. At the present day the coal is heated for several hours in an electric resistance furnace. Carbides of the various metallic constituents of the ash are formed. When the temperature is carried still higher these carbides are decomposed, the silicon, iron and aluminum vaporized and the graphite left.

The manufacture of graphite electrodes, plates and various other shapes is really a branch of the carbon electrode industry. The raw materials for graphite articles and graphite powder manufacture are the same, being essentially coal and petroleum coke. If an electrode is destined to be graphitized and used as a graphite electrode, this fact must be taken into account at the very beginning of the process of manufacture, in fact, in the selection of the raw materials themselves. Raw materials of a quality perfectly suitable for carbon electrodes might not be at all suitable for graphite electrodes. For this reason an entirely satisfactory graphite electrode cannot be made by graphitizing an ordinary carbon electrode such as is used in electric furnaces; neither can a carbon electrode made specifically for graphitizing be used successfully as a carbon electrode in ordinary electric furnaces. The binders are also of the same types, being usually pitches, sometimes mixed with tars and occasionally oils. The material before shaping is calcined in the

same manner as the raw materials for amorphous electrodes. Pulverizing, mixing and shaping practices follow the lines previously indicated under electrodes. With very few exceptions artificial graphite electrodes are formed by extrusion. This method is easily adaptable to the manufacture of any modification of circular or rectangular cross section articles, providing the cross section is uniform throughout the length of the piece. Extruded electrodes have less porosity and greater mechanical strength than those formed by molding. Experience has shown that as the ratio of width to thickness increases the difficulty of manufacture increases, due to extrusion scrap, increased breakage and other causes. Consequently, relatively thin plates are necessarily more expensive than those of more nearly square cross section.

The essential difference between the manufacture of graphite articles and those of amorphous carbon occurs in baking. Graphite electrodes are baked in either of two ways. In one method graphite electrodes are ordinarily baked in the same manner as are amorphous electrodes in the same types of furnaces, usually of the coal or gas fired modifications. They are afterwards graphitized in electrical resistance furnaces. The second method consists of loading the shaped green article directly in the graphitizing furnace, baking it and graphitizing it in the same place.

Graphitizing furnaces may be considered as modifications of the standard amorphous electrode baking furnace. Their general construction is the same, the furnaces being about the same length, but with heads somewhat narrower and not as high. In the Acheson furnace, shown in Fig. 14, busbars, rising through the floor, are connected directly to the electrode heads, the connection being broken at these points when the furnace is off power. Loading and unloading are accomplished as with the amorphous carbon baking furnace, with the exception that a central core of larger cross-sectional area is used. Power consumption is much higher, being from 3 to 5 kw.-hr. per pound of graphitized carbon. Temperature control, being relatively difficult above 1,100°

C., is normally dispensed with, and the run of the furnace is regulated by power input. Packing material, sidewall and top insulation are thicker, for the furnace reaches a temperature of approximately 2,000° C.

The theory of the production of graphite is that carbides are formed by reaction of the amorphous carbon and the metallic and siliceous oxides present as impurities. The furnace, however, soon reaches the temperatures at which these carbides are decomposed, distilling off the metals and metalloids, leaving graphite behind as a result of the decomposition. Packing dust used in graphitizing furnaces becomes contaminated much more readily than in amorphous baking furnaces. The packing material layers serve as a cold blanket, in which the metallic and siliceous vapors condense, re-forming carbides to some extent in the layers nearer the center of the furnace and oxidizing in the cooler outer portions. It can be seen, then, that relatively impure material might be used in the manufacture of very pure graphite electrodes inasmuch as nearly all of the contamination is volatilized. It is a question if it would be advisable to do so as the volatilization of large amounts of impurities would eventually impart a very high degree of porosity to the electrodes. Acheson electrodes are made of selected materials, the purity of which is carefully watched.

A graphite furnace cycle is approximately as follows: Loading, 1 to 2 days; on power (depending upon capacity of transformer and size of furnace), 3 to 6 days; cooling, 20 to 30 days; unloading, 1 to 2 days, giving a minimum cycle of 25 and a maximum of 40 days.

Graphitized carbons are generally cleaner than amorphous electrodes when taken from the furnace; they have fairly smooth surfaces and require relatively little further work on them. The reason is that the temperature rise is so great that the ash and vapors from the binder are distilled away from the carbons very rapidly and are condensed in the insulating packing material layers only and not in the packing dust between the carbons. The removal of the lay-

ers of insulating packing material is more difficult than in the case of the amorphous carbon furnace.

Well-graphitized electrodes have approximately one-fourth the resistivity of the corresponding amorphous carbon. Graphite carbons run from 0.00032 (Acheson, completely graphitized) to around 0.00080 ohm per inch cube

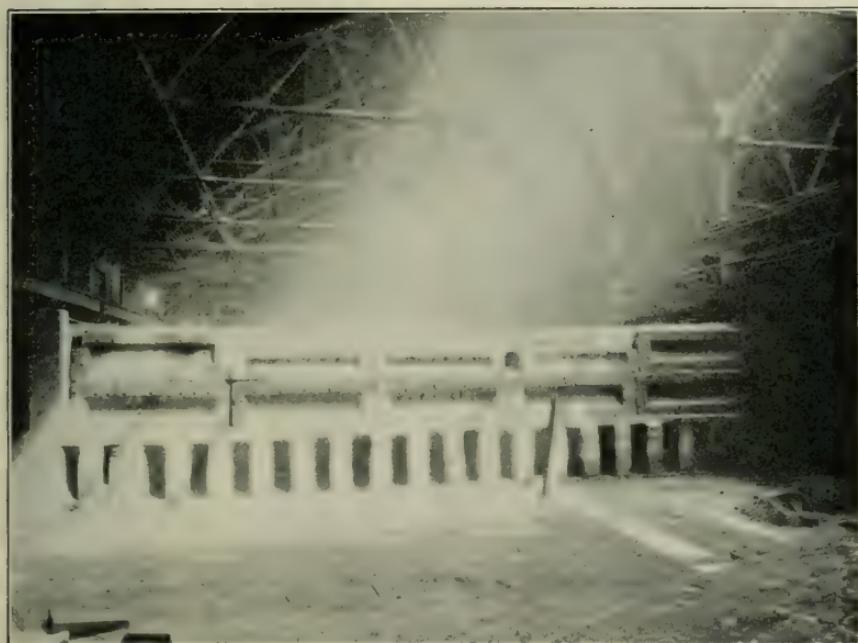


FIG. 14.—A MODERN GRAPHITE FURNACE
(Courtesy Acheson Graphite Co.).

(partly graphitized carbon, commonly called overbaked amorphous), depending upon the completeness of the graphitization of the amorphous carbon. The greater the conversion to graphite the lower the resistivity.

In the manufacture of graphite powders the same type of furnace is used but the raw material is ordinarily anthracite coal, sometimes even coal waste or culm or petroleum coke. The material is crushed fine and loaded in bulk into

the furnace. On the passage of the current innumerable small arcs are formed between adjacent particles. The mass becomes incandescent and is allowed to remain so until all the impurities have been vaporized, the length of time required being dependent upon the purity of the raw material.

It is a natural assumption that the higher the carbon content of the charge the greater will be the amount of graphite obtained. This would be the case provided the carbon were altered directly to graphite. Such alteration, however, does not take place in actual practice. What actually occurs is an indirect alteration consisting in the dissociation of metallic carbides. Fitzgerald,⁴ writing in 1904, states that the quantity of graphite obtained is considerably greater and a better product is secured when a coal is used that contains a large amount of foreign mineral substance. There is considerable doubt that, under the present day practice, the quantity of ash present in the raw materials has the influence on the quantity of graphite obtained, as here stated. No matter what the ash content of the raw material — and all practical raw materials contain some ash — the process is so conducted that the carbon is converted completely into graphite: that is, there is no question of a mixture of graphite and non-graphitic carbon in the finished product; it is all graphite. The amount of ash in the raw material does, however, influence the physical properties of the finished graphite. Acheson's experiments showed that a relatively small amount of the carbide-forming materials can bring about a conversion of a large quantity of carbon into graphite. This amount is much less than what is theoretically required. An anthracite coal containing 5.78% ash, which ash is largely silica, alumina and iron oxide, is converted into practically pure graphite containing only .03% ash. The table below shows the changes resulting in amorphous carbons first baked in gas-fired furnaces and then graphitized. The apparent density is considerably increased and the resistivity markedly decreased.

⁴ Monographien über Angewante Electrochemie, vol. XV. Halle 1904.

TABLE I

<i>Amorphous Carbons</i>		<i>Graphitized Carbons</i>	
<i>Apparent Density</i>	<i>Resistivity (ohms per inch cube)</i>	<i>Apparent Density</i>	<i>Resistivity (ohms per inch cube)</i>
1.53	.00172	1.58	.00056
1.56	.00158	1.62	.00057
1.56	.00161	1.65	.00051
1.52	.00170	1.64	.00047
1.57	.00162	1.65	.00042
1.54	.00146	1.65	.00046
1.57	.00131	1.64	.00035

In Table II. figures are given for ash, silicon, iron and copper on certain green electrodes which were first converted into amorphous carbons and later on graphitized. The ash content of the green electrode, inasmuch as in baking only the binder is removed and none of the ash constituent volatilized, has increased when found in the baked electrode; but inasmuch as in graphitizing the ash constituents are volatilized, the ash content is shown to be markedly decreased in the graphitized electrode.

TABLE II

		<i>% of Total Ash</i>	<i>% Ash Removed</i>	<i>% Si</i>	<i>% Si Removed</i>	<i>% Total Fe</i>	<i>% Fe Removed</i>	<i>% of Total Cu</i>	<i>% Cu</i>	<i>% Cu Removed</i>
1. Green Electrode		9.89		0.20		0.12		0.38		
1. Amorphous Baked Carbon		10.72		0.23		0.19		0.33		
1. Graphitized Electrode		0.83	92.0	0.03	85.0	0.03	75.0	0.03	92.0	
2. Green Electrode		7.79		0.06		0.08		0.18		
2. Amorphous Baked Carbon		7.92		0.20		0.17		0.20		
2. Graphitized Electrode		0.89	88.3	0.02	66.4	0.02	75.0	0.04	77.5	

The commercial characteristics of good quality Acheson graphite electrodes are given below —

Weight in lbs. per cu. in.0574
Weight in kgs. per cu. cm.0016
Specific resistance in ohms per in. cube00032
Specific resistance in ohms per cm. cube000813
Density	2.25
Temperature of oxidation in air	660° C
Percentage of graphitic carbon	98.8 to 99.5

The alteration of carbon to graphite is a complete one. When the material is treated with potassium chlorate and nitric acid, no trace of amorphous carbon is found. In respect to the above test, however, and also Berthelot's definition as to what constitutes graphite, — that is, a form of carbon that yields graphitic acid on oxidizing at a low temperature, — it should be noted that all graphite made by furnace methods but from various materials does not exhibit the same characteristics. Electrodes made from soft coal and petroleum coke show decided differences in their properties. The former are hard and brittle. They mark paper with difficulty and do not become shiny on rubbing. They are soon consumed when ignited in the air. Their decomposition is rapid when used as anodes in solutions containing sulphuric acid. Petroleum coke electrodes, on the other hand, have characteristics the reverse of those described for electrodes made from soft coal. The specific gravity of electrodes made from petroleum coke is 2.20 as against 2.05 for those made from soft coal. They both conform to Berthelot's definition of graphite, yet they are decidedly different in most of their physical properties.

The diversity of forms in which amorphous carbon and graphite occur seems to be limitless. Even the expressions used to distinguish forms of carbon that yield graphitic acid from those that do not, — namely, graphite and amorphous carbon, — do not correspond to fact. Many artificial types possess crystalline structures, while a number of natural

graphites are amorphous. The graphite formed from carborundum decomposition appears to be finely crystalline but it is really amorphous. Anthracite coal produces graphites which are very variable in character, depending upon the grade of coal used. Some are soft and lustrous, others hard and matte. Their specific gravities range between 2.20 and 2.25. They are more resistant to the action of potassium chlorate and nitric acid than is Ceylon graphite, but practically all of the artificial types burn more rapidly in air than does Ceylon graphite.

The cleaning, testing, machining and shipping of artificial graphite articles are quite analogous and similar to that given in detail under amorphous electrodes. Fig. 15 shows a number of graphite electrodes for electrothermal work. The ease of machining graphitized electrodes is too well known to require any extensive discussion. They are easier to machine than the softest iron and may be finished with the same degree of nicety. Threads can be cut, holes drilled and tapped or the electrodes surfaced, sawed or shaped in any way desired by the use of ordinary wood-working tools.

Graphite electrodes are manufactured in any size and shape desired. For ordinary use, the cylindrical or square shapes satisfy all requirements. Graphite electrodes may be obtained with any cross section between the limits of $1/16$ in. to 18 in. in diameter and with any length up to 60 in.

Because of the inherent difficulty of manufacturing plates of great width by the extrusion method and the relative inferiority of molded plates for electrolytic work, it is often found much cheaper, as well as more convenient, to obtain wide electrode surfaces where necessary, by placing two or more graphite plates edge to edge and connecting them with graphite dowel pins.

The method used for joined electrodes for continuous feed is of the straight separate nipple type. The size of the nipples is so proportioned for each size electrode as to give a maximum mechanical strength to the joint as a whole. This method is the same as that used for amorphous elec-

trodes. Because the physical properties of Acheson graphite permit easy and accurate machining, the joint is made to fit

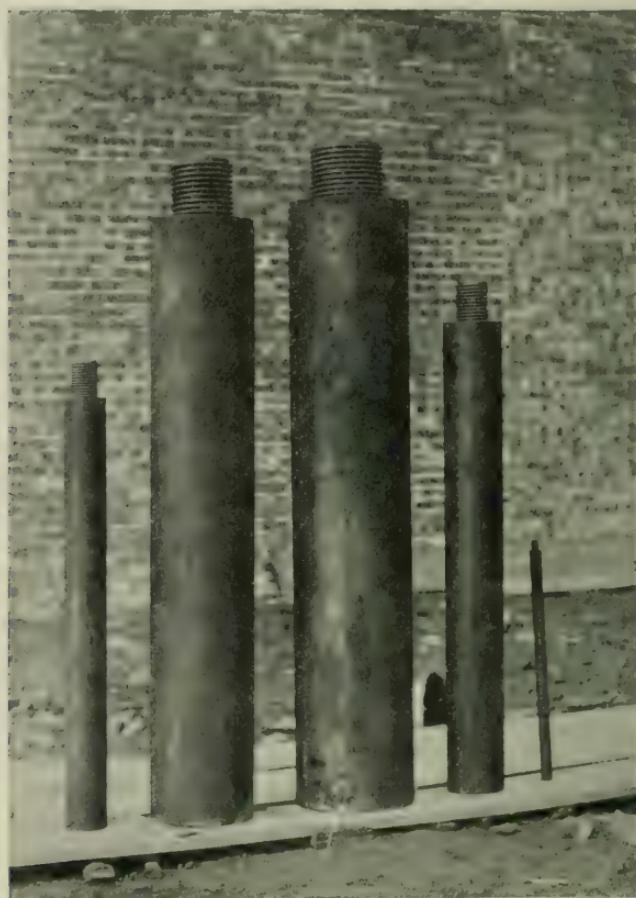


FIG. 15.—GRAPHITE ELECTRODES OF VARIOUS SIZES,
THREADED FOR CONTINUOUS FEED

(Courtesy Acheson Graphite Co.)

so closely that the use of a paste or filler of any kind is not necessary.

In certain cases, such as those of electric steel furnaces, low resistivity of the electrode is of great importance. Mod-

ern electric steel furnaces are very high powered compared to the old ones and use very high currents. For this reason the I^2R losses in the electrodes become of extreme importance as very high currents are employed. Amorphous electrodes may be used with current densities of the order of 40 amperes per sq. in. cross section, while graphite electrodes allow the use of current densities of about 300 amperes per sq. in. with electrodes 2" in diameter, to about 100 amperes per sq. in. with electrodes 14" in diameter. The use of graphite electrodes allows the furnace operator to employ smaller cross section units than those necessary when amorphous carbons are used. In many cases the amorphous carbon electrode becomes unwieldy because of its necessary size.

As an example, the I^2R losses were calculated in a typical three-ton Heroult furnace. When operating at 1300 K.W., three phase, and drawing 7200 amperes per phase, the I^2R loss with 14" amorphous carbon electrodes amounted to about 125 K.W., and with 10" graphite electrodes, to about 66 K.W. In the case of a six-ton Heroult furnace, three phase, operating at 1700 K.W. and drawing 10,000 amperes per phase, the loss with 17" amorphous carbon electrodes was about 170 K.W. and with 12" graphite electrodes, about 87 K.W. While it is true that a large portion of the heat generated in the electrodes by these I^2R losses is delivered inside the furnace and therefore contributes to a certain extent to the furnace temperature, nevertheless such heat is never generated where it is most desired, — that is, at the arc.

In a large number of cases, a very high degree of purity in electrodes used in furnaces may not be of importance. In steel manufacture, however, the sulphur content of the electrodes is of great importance and it may be desirable, to prevent contamination of the melted material, to use graphite electrodes which are of very high purity instead of amorphous electrodes liable to contain sulphur.

The question as to whether amorphous electrodes or

graphite electrodes are to be used in electric furnaces is satisfactorily settled only by a balancing of all the economic conditions resulting. While smaller graphite electrodes may be used, their cost is greater than those of amorphous carbon. This subject is discussed under carbon electrodes to which the reader is referred.

Acheson graphite is practically the only form of carbon used as electrodes in electrolytic work such as the manufacture of caustic, chlorine, the alkalies, sodium and similar commercial materials. In order to be satisfactory for this work, the material has to be graphitized after shaping. Graphite articles, made of graphite originally held together with a binder and then baked, always fail at the binder, disintegrating very rapidly when in use. In the United States there are one or two installations for chlorine and caustic manufacture employing platinum anodes, but in practically all other cases graphite electrodes are employed for this purpose. Amorphous carbon electrodes are ordinarily decidedly unsatisfactory for electrolytic work. Amorphous electrodes were formerly used to a considerable extent in Europe, but this is hardly the case at the present time. Except for one relatively small installation in England, where pieces of retort carbon are still used as anodes, there are no important electrolytic installations which are not using graphite electrodes. Abroad the use of other materials, such as retort carbon and platinum, has practically entirely disappeared.

When graphite is made for lubrication by the Acheson process, purities of 99% or better usually result. For lubricating purposes it is ground to 200 mesh and air floated. This air floated graphite is termed disintegrated graphite and from it the so-called deflocculated graphite is prepared by a process involving the addition of tannic acid. In preparing this deflocculated graphite for commercial use, it is first suspended in water and the mixture run into large settling tanks where it remains for several days. It is then decanted and passed through a filter press fitted with rub-

berized canvas sheets. Pastes are thus obtained containing approximately one half graphite and one half water. In order to replace the water by oil, the paste is ground in a pug mill and continuous small additions of oil are made until the water eventually is completely displaced by oil. This paste of graphite and oil, sometimes mixed with lighter

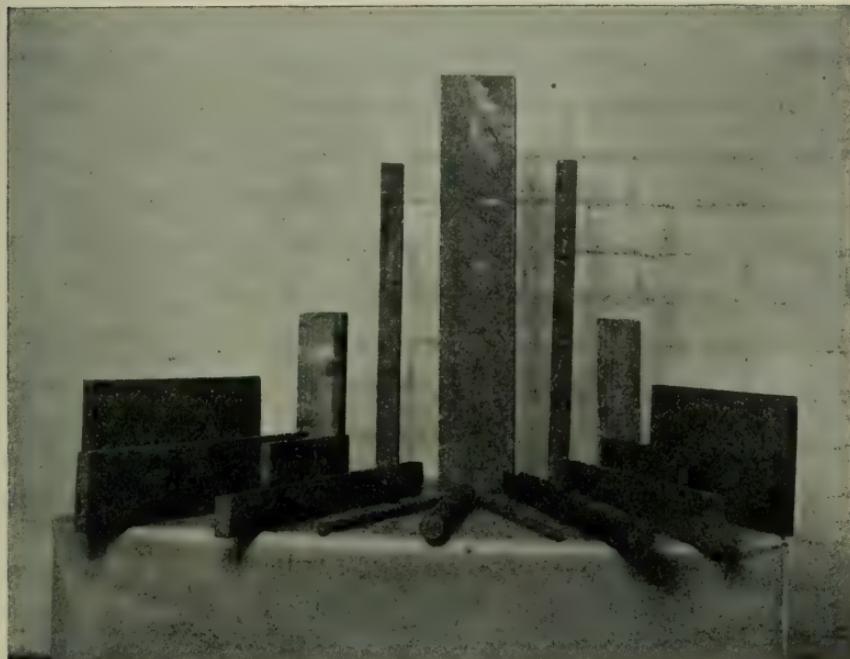


FIG. 16.—SIZES AND SHAPES OF GRAPHITE USED FOR ELECTROLYTIC CELLS

(Courtesy Acheson Graphite Co.)

oils such as kerosene, yields the Acheson lubricating product known as Oildag, while the mixture of water with the paste of graphite and water is termed Aquadag. Acheson⁵ states that deflocculation is produced by treating the graphite in the disintegrated form with 3% to 6% by weight, on the basis of the graphite treated, of tannin in water solution.

⁵ J. Franklin Institute, 164, (1907) p. 376.

The results are more pronounced when the mass of graphite, water and tannin has been pugged or masticated for a considerable time. If water, graphite, a drop of ammonia and a little gallo tannic acid be shaken together in a test tube, enough of the graphite will remain suspended in the liquid to give it a black color. Most of it, however, will settle out and prolonged mastication is necessary to cause complete suspension. These colloidal solutions produced pass through filter papers without the removal of the contained graphite. One per cent of graphite makes the liquid so thick that it runs through the filter paper slowly. Reduced to .2 of a per cent, it goes through more quickly. The addition of minute amounts of mineral acids, such as hydrochloric, causes the graphite to flocculate so that the mass will no longer pass through filter paper. This graphite, even after such flocculation, is so fine that when its particles are dried it forms a hard mass which is self-bonding, like a sun-dried clod of clay.

Since graphite rods are so readily machined, many small articles such as disks, bushings, washers, contacts, etc., can be made from solid rods or blocks far more satisfactorily than by molding. Graphite molds, crucibles and testing vessels used in melting point determinations, as well as equipment for use in casting the precious metals, are ordinarily made from graphite blocks by machining.

Artificial graphite is extensively employed in dry batteries of the Leclanché type, used for starting, ignition and particularly radio batteries, where it serves to give conductivity to the mass of manganese dioxide employed as a depolarizer. Formerly the powdered carbon in a dry cell, amounting to nearly one half of the total solid ingredients, consisted largely of coke, retort carbon, petroleum coke, ground carbon rods and electrodes, all of which are considerably cheaper than graphite of the required purity.

Some of the large battery manufacturers especially calcine carbonaceous material to be used for battery filling in electric furnaces so controlled that they may vary the percentage of graphitization caused to take place and in this

manner control the resistivity of the product. A very large percentage of the dry batteries manufactured in the United States are filled with artificial graphite with the addition of small percentages of natural flake graphite. The natural graphite is employed as a lubricant on the bobbins and machines used for molding the fills employed in the small size batteries for radio work, where a number of cells are connected in series to give the required voltage.

Artificial graphite finds employment to a more or less wide extent in all those fields where natural graphite is employed except that of graphite crucible work. Artificial graphite is extensively employed in the manufacture of brushes for electrical machinery. This application will be discussed separately in the chapter on brushes.

CHAPTER V

GRAPHITE CRUCIBLES

THE materials for crucible manufacture, while differing in some minor details, are practically the same everywhere. The preparation of the mixture and the proportion of the graphite, clay and grog or sand entering into it are the jealously guarded secrets of the individual makers. In exceptional cases where high refractory qualities are demanded, the graphite percentage may be as high as 80 and over. Such high proportions, however, result in structurally weak crucibles.

The graphite, whether it be Ceylon or flake, undergoes considerable preparation at the crucible works, in addition to that received before shipment. Ceylon graphite is preferred above all others. The standard crucible grades are lump numbers 1 and 2, chip numbers 1 and 2, and dust. These vary considerably in their carbon content, ranging from as high as 92% in the case of lump number 1, to 70% to 75% for dust. The price varies according to the type of graphite, its physical form and its carbon content.

The lump and chip grades are ground and selectively screened. The graphite used in crucible making is a blended aggregate of various sized particles. The very fine or dust screenings resulting from grinding are not suitable for crucible manufacture and are disposed of as facings and other uses.

The grading or curing of the graphite at the compounds in Ceylon is entirely manual. The impurities are chipped out of the lump material. Lump number 1, or ordinary lump, is therefore the purest material shipped.

Flake graphite, though purchased on a basis of approximately 90% carbon content and a flake size of 20 to 90 mesh,

is usually rescreened previous to use. In some cases it may even be reground in burr stone mills. Flakes of more than ordinary size, that is, much above 20 mesh, are not desirable as they decrease the density of the crucible and detract from its strength.

The clay is first kiln dried at a temperature of 120° C. until moisture free. It is then ground in stamp mills, in some cases in burr stones or tube mills or edge runners, and then screened to remove lumps and foreign matter.

Sand is sometimes used to the extent of 10% in mixtures made for steel melting. Usually only clean, fine-grained quartz sand is employed. The sand serves to diminish shrinkage of the crucible body. The cleaned and sized materials are weighed and charged into mixers together with water. Mixers are of various types. One commonly employed is of the vertical type with bladed shafts continuously pressing the material out at the bottom of the mixer, causing it to pass through a vertical cylinder at the side and feeding back into the mixer at the top. Pug mills are also used for further mixing and eliminating air from the batch. The mixed material is made just softly plastic by the addition of water and kneaded to a uniform consistency. It is then set aside in a clay cellar to age. Sometimes before being worked up in the pug mill, the dry materials may be sprinkled with water and left to become thoroughly impregnated with moisture. The lumps of kneaded material are sometimes allowed to season for several weeks. When the mass commences to show a dry surface crust, it is again worked up in a pug mill until all parts are homogeneously mixed.

The material after seasoning is ready to be worked up into crucibles. In American practice, mechanical means are used almost entirely except for special shapes made only at infrequent intervals. The appliance used for throwing the crucible is styled a "jigger" or "olley." The operation is termed "jigging."

A given weight of the mixture is taken, kneaded by hand

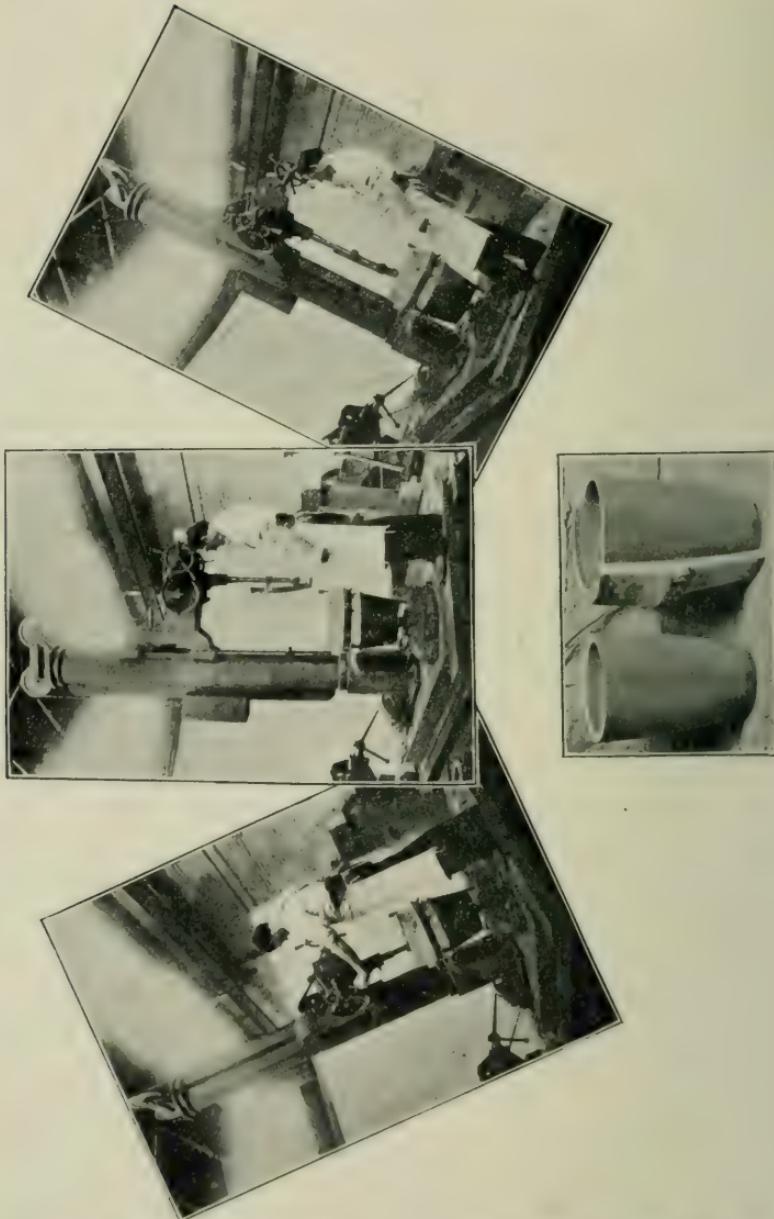


FIG. 17.—METHOD OF JIGGERING CRUCIBLES
(Courtesy Crossley Machine Co.)

into a ball and placed in the mold. The mold stands on a base board fixed on a revolving table. The mix is tamped down flat with a wooden pestle and the table set revolving.

A small curved arm known as the rib or jigger, attached to a vertical shaft, is lowered into the mold. Figure 17 shows the method of operation. The jigger arm is stationary, the mold with the crucible mixture revolving. On meeting the clay mixture, the rib forces or squeezes it upward between itself and the wall of the mold. The rib is lowered at a distance from the mold required to form a crucible wall of the desired thickness, and to a depth that will give the proper bottom thickness. The necessary adjustments can all be readily made on the machine. Throwing the crucible then becomes almost automatic. Obviously the same type of set up may be used for crucibles of various sizes. The weight of clay mixture necessary to form a pot of certain size has been determined by previous plant practice. There is then practically no surplus forced up out of the mold. The top edge of the crucible is smoothed off by hand. The pouring lip is made by cutting out a small section with a tool especially made for the purpose.

The molds are made in two vertical halves. The sections are provided with tongue and grooves to insure proper joining when they are set up. Molds are made by building up a sheet iron casing around a solid model of the size and shape of the exterior of the crucible to be made. A space equal to the desired thickness of the mold wall is left between the model and the casing. Two metal strips are inserted in this space half way around the periphery so as to divide the space into two equal halves. Plaster of Paris is then poured in, the solid model being first well soaped to prevent sticking. When this is set, the mold is removed and finished to the exact size. The mold is open at the bottom and rests on a mold board during formation of the crucible. In use the two halves of the mold are held together by means of flexible steel straps or rings provided with brass clamps for tightening.

After the crucibles are finished they are inspected on a hand jolley and any necessary removal of imperfections done at this time. The crucibles remain in the molds for a few

days to harden sufficiently for handling. They are then removed and piled in tiers in large drying rooms where they air dry for 4 to 9 weeks according to the size and shape of the crucible. From here they are taken to other drying rooms supplied with hot air at 150° where they are dried for about a week at this temperature. The shrinkage during drying, measured along the diameter of the pot, may amount to as much as $\frac{1}{2}$ to $\frac{3}{4}$ of an inch. After drying the crucibles are placed in large muffle kilns of the type as shown

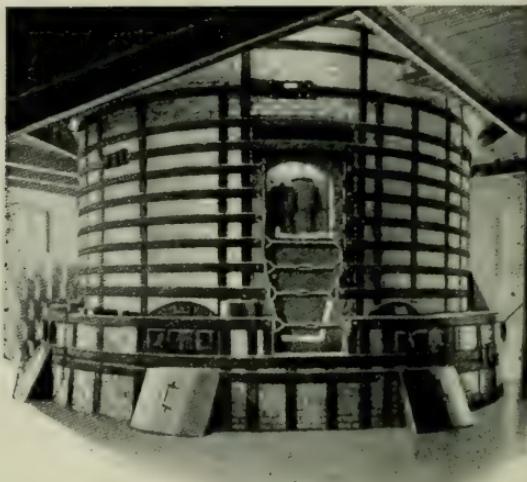


FIG. 18.—A MUFFLE KILN
(Courtesy Jonathan Bartley Crucible Co.)

in Figure 18. These kilns are 15 to 20 feet in diameter, usually coal fired in small grates on the outside of the kiln. These are shown in the illustration at the places where steel doors are leaning against the kiln. The crucibles are baked — or rather, fired — to a temperature just a little above the dehydration of the clay. This temperature point will vary from 1500 to 1800° F. The firing consumes from 30 to 50 hours after which the kiln is allowed to cool off for 5 to 6 days before unloading. Muffle kilns are preferred to the open, down-draft type as saggers are eliminated in the

former case and a more uniform heating is effected. It is claimed that oil fired kilns do not allow uniform heat penetration to the center of the mass being fired and are therefore not so successful as coal fired kilns.

The requisites of a good graphite crucible are strength, refractoriness, good heat conduction, the capability of being used for many meltings of metals, and resistance to the action at high temperatures of the molten materials with which it comes in contact. The graphite contributes toward the refractoriness and heat conductivity of the mass. At the same time it produces a smooth surface for pouring. The function of the clay is that of a bonding material which makes possible the forming of the crucible and the cementing of the graphite flakes. At the same time it covers them and prevents their oxidation.

The refractory quality of a crucible is much misunderstood. It is not so difficult to provide for refractory quality alone as for the other requisites of a good crucible. The range of refractoriness is very great. The crucible giving good service at the temperature of nickel fusion is not well adapted for service in spelter castings. The mixture has to be varied according to the service required.

The graphite in the wall of the crucible begins to oxidize at about 600° C. This rate of oxidation increases with the temperature and varies with the composition of the furnace gases. The life of a crucible depends largely on the non-oxidation of the graphite. The glaze on the outer surface delays this oxidation, but the glaze depends on the refractoriness of the crucible mixture. Hence if the material be too infusible, the life of the crucible is very much shortened; but if it be too fusible, it softens and fails to protect the graphite. Some users coat the outside of a crucible with a mixture more fusible than the crucible wall itself. If the first heat to which a crucible is subjected is but high enough to produce this protective glaze, its life at lower subsequent heats is much prolonged.

Graphite crucibles may be classified according to the kind

of metal to be melted, the kind of fuel to be used, and the different types varying in shape and in composition. The principal division is in steel crucibles and in brass crucibles. Other metals or alloys are melted in one or the other of these two types. According to the class of fuel used, crucibles may be divided into gas, coke, coal and oil.

The general shape of all those made in the United States is that of an ovoid cut off flat at each end. The steel crucibles are of nearly the same diameter at top and bottom and the bilge or greatest diameter is little more than half way up. Brass crucibles are of the same general shape save that the top diameter is considerably greater than the one at the bottom. The ratio of diameter to height is less in steel than in brass crucibles. This is more pronounced in the foreign makes than in the American types. Many special shapes are made to suit special work or furnaces. The more usual crucible sizes are designated by numbers and shapes.

Another and larger type of graphite crucible is the retort used in the distillation of zinc in silver refineries. These range from 30 inches to as long as 72 inches in some cases, with bilges from 16 to 40 inches. Some are used in furnaces of the tilting type, while others are employed in the more general stationary furnace. Their general shape is that of a bottle flask.

The number of heats that a crucible may be expected to stand is dependent essentially on the materials of its composition, the care taken in manufacturing, and the handling it receives in service. No matter how well a crucible may have been made, it will have its life very materially shortened by careless handling. Graphite crucibles, like all other materials containing clay, are hygroscopic and should be freed from moisture by gently heating before being put into use. Disregard of this precaution causes the loss of thousands of crucibles annually.

Improper fuel is extremely detrimental to crucibles, especially those giving off gases high in sulphur. These penetrate

the crucible walls and cause serious "alligator" cracks to develop. This is especially pronounced in the case of wet fuel or imperfect combustion with oil or gas.

The various kinds of work in which graphite crucibles are used as the melting vessel include malleable castings, small iron castings, crucible cast steel, all kinds of copper and zinc alloys, spelter castings, file tempering, and precious metal melting and refining. Oblong, square and round shapes are used in liquid brazing and as calcining trays or boxes for material requiring careful, even heating without exposure, such as pencil leads, incandescent carbon filaments and so forth.

Graphite crucibles are not so porous as those of clay and thus do not absorb so much of the melted metal as the latter. For this reason they are preferred in the melting of precious metals.

It is a decided question as to whether the graphite crucible industry will expand largely in the coming years. The decided tendency as seen some years ago toward the adoption of the electric furnace with its manifold advantages in various metal industries, will prevent expansion of crucible melting. Crucible steel has almost become entirely a misnomer, as almost all so-called crucible steel is made in electric furnaces. There are, however, many industrial applications, usually small scale in size, which will very likely always require crucibles. The pro and con of crucibles versus gas fired hearth furnaces or electric furnaces has been much discussed in the last decade. The advocates of both sides are equally positive in their conclusions as to the relative merits of either method of operation.

CHAPTER VI

OTHER GRAPHITE REFRAC TORY PRODUCTS

A LARGE variety of refractory articles used in foundry work and metal smelting other than crucibles are made from mixtures of graphite and refractory clays. These articles include crucible covers, stopper heads for open hearth steel ladles, pouring nozzles, stirrers, rings, jackets, skimmers, dippers, phosphorizers, crucible extension tops, pyrometer shields, and miscellaneous furnace articles.

Many special forms of crucibles are used in industry. The tempering crucibles for files and tool steel are usually cylinders, the manufacture of which is conducted in the same manner as that of graphite crucibles. The tempering crucibles are filled either with molten lead or hardening salts and the heated steel from the forge immersed in these tempering baths so as to effect a gradual cooling.

Brazing crucibles are of many different forms and shapes, usually having straight sides sloping in a V shape toward the bottom. Extension tops or funnels are used on top of crucibles to allow the addition of a larger charge of turnings or chips of metal. This reduces the necessity of frequent additions of small quantities.

Pyrometer shields are usually closed-end cylinders made entirely of graphite without a clay bond. These serve as protections for the wires of thermo-electric pyrometers. Graphite crucibles used in pyrometer calibration are ordinarily cut or machined out of solid pieces of artificial graphite. Pyrometer shields are usually made in the same manner also from artificial graphite.

Phosphorizers are made of the same mix as crucibles.

They are used to introduce phosphorus into ladles of molten copper, tin or bronze in the manufacture of the corresponding phosphor metal. They are ordinarily cylinders with a truncated cone top section made in one piece. Holes are provided at the top and bottom. An iron rod is fastened in the hole in the neck and the phosphorus, securely wrapped to prevent spontaneous ignition, is placed in the chamber. It is held in place by a wad of paper. The phosphorizer is then plunged into the molten metal, being held there until it is judged that all of the phosphorus has been absorbed by the metal. Being of the same composition and characteristics as crucibles, phosphorizers require annealing before use to prevent cracking.

In a number of industries small boxes made of graphite and clay mixtures are used as containers for materials undergoing heat treatment, baking or burning.

Skimmers and stirrers are straight sections or curved sections or molded or extruded rods mixed, baked and handled in the same way as graphite crucibles. Dippers and ladles, the term being sufficiently descriptive of the article, are made in many shapes and sizes.

CHAPTER VII

LUBRICATING GRAPHITE

THE very low coefficient of friction of graphite is retained under practically all working conditions. It is soft and readily adheres to metallic surfaces, even under light pressures. Its property of filling in the pores of a metal makes it very valuable for lubricating work. The surfaces of bearings when lubricated with graphite become covered with a veneer of the material, which reduces the bearing coefficient of friction to practically that of graphite itself. Graphite is remarkably resistant to most chemical and corrosive actions. The veneer it forms on bearing surfaces thus tends to protect these from the action of corrosive solutions or vapors. This applies particularly to cylinder lubrication where high pressure steam, oil or gas is used. Oil and grease lubricants under these conditions tend to lose body or to char or vaporize under the action of the heat and the gases to which they are exposed. In heavy bearings, oils and greases show a tendency to squeeze out from between surfaces. As a result the metal parts come in contact and are subjected to wear. Graphite, forming a coating on both metal surfaces, allows a graphite contact instead of a metal contact to be secured.

For ordinary lubrication in open bearings, slides, gears and similar places, the graphite is commonly mixed with oil or grease. There are a great variety of such compounds on the market, each having according to their manufacture unusual and specific properties. Many of them are designed for work under special conditions such as exposure to salt water, acids or alkalies, in dredges, winches and mining machinery, or at different temperatures where varying degrees of viscosity are required.

In steam and gas engine and compressor lubrication, dry flake or powdered graphite is often used in addition to oils and greases. In marine engines, cylinder lubrication by graphite is quite advantageous as this method reduces the amount of oil which finds its way into the condensers and boilers. Graphite is largely used in pipe joint compounds for lubricating and sealing the threads and flanges of various types of piping, as well as various machine parts which are to be more or less permanently in place.

It is claimed for the amorphous and artificial graphites that they are both purer and more capable of being reduced to an impalpable powder. As a result, they will remain in suspension in oil more easily than the natural flake graphite. Natural flake graphite, however, no matter how finely ground, will retain its flake or scale form so that when it is fed in between bearings a scaly layer eventually results. Bierbaum¹ states that "the value of a so-called permanent suspension of graphite in oil is more fanciful than real for the reason that, in all such attempts, the graphite is ground to such an extreme degree of fineness that this very fineness mitigates against its being useful. In a bearing properly constructed, lubricated and in operation, the bearing surfaces are completely separated by the oil film and the extremely fine particles of graphite simply float in the film, exerting no appreciable effect either beneficial or otherwise.

"The time, however, when graphite can be of benefit and perform its only and supreme function is when the oil film between the bearing surfaces is destroyed and the graphite serves as a solid lubricant. The graphite is carried between the bearing surfaces by the oil, and in the same manner, when the oil film is destroyed by being squeezed out, the graphite particles are carried along with the oil from between the bearing surfaces until the film is reduced to a thickness corresponding to the dimensions of the largest particles of graphite which at this stage will be arrested and held between the surfaces. Upon the complete destruction of the

¹ Iron and Coal Trades Review, Jan. 1918, p. 718.

film, these particles so held are crushed and embedded into the grain and pores of the surfaces, and thus are made to perform their function of solid lubrication. It is evident that the smaller the particles are, the less will be the amount of graphite so intercepted between the bearing surfaces; therefore, a given amount of graphite is most efficient if it exists in particles of the largest possible size. The more nearly permanent a graphite suspension is, the more nearly does it approach the colloidal state and the more completely is it carried out from between the bearing surfaces when the oil film is being destroyed."

Chemical analyses of graphites for lubrication can only give information when the results are co-ordinated with experience. Inasmuch as the percentage of amorphous graphite in some varieties is high, the carbon content of graphite is not an indication of its lubricating value. Carbon not completely graphitized can at best only be classified as an inert.

Graphite powder is employed in lubricating surfaces where oil or grease might be detrimental and liquids of any sort are to be avoided.

There is considerable competition between natural and artificial graphite in the lubrication field. The Acheson Company puts out so-called deflocculated graphite in their Oildag and Aquadag lubricating compounds. The deflocculated graphite is claimed to be graphite reduced to the molecular form, the finest possible state of subdivision. It is prepared from artificial graphite finely ground and air floated. The deflocculated material is prepared by the addition of tannic acid. In order to produce an oil suspension it is first necessary to make a paste of graphite and tannin in water, oil being gradually substituted for the water during working, and the oil paste finally diluted to the desired consistency.

CHAPTER VIII

FOUNDRY FACINGS

THE term " facings " in general use in a foundry is applied to the facing sand which forms a layer about an inch thick around the pattern. In its specific sense, it relates to those materials which are used to give the insides of the molds a smooth finish so that the castings part freely and cleanly on cooling.

Graphite is the most important material used for foundry facings. More graphite is used in the making of this article than is consumed in any other manner, with the exception of crucible manufacture. Foundry facings are practically the only market for the low grade dust graphite from the refining mills. This material runs 40 to 70% carbon. There are many foundry facings on the market running 60 to 70% carbon but a considerable percentage of this is non-graphitic.

Foundries do not generally manufacture their own facings but secure them from supply houses having specifically equipped plants for grinding, mixing, and otherwise treating the whole variety of material used in foundry work. The preparation of graphite for facings involves grinding in tube mills, ball mills or pebble mills, and screening or air floating the product. It costs too much to air float some grades of facings which sell for three to four cents per pound. These grades are only ground in mills and screened. This is in addition to the preliminary drying and crushing required for crude ores.

Graphite itself possesses no adhesive properties. Refractory clays are therefore added as bonding agents. The binder absorbs a certain amount of moisture from the mold, thus holding the facing in place. When the clay is calcined by the molten metal, the facing is rendered somewhat po-

rous, thus allowing moisture and occluded gases to escape. Proper proportion as to the graphite and binder is important, since if there be too much of the latter stripping becomes difficult, and if too little, the graphite runs before the metal or floats on it.

Many carbonaceous materials such as graphite, coke, charcoal, in finely ground form, are used as facings. They are, in foundry parlance, termed "blackings" in contrast to silica, talc, soapstone, etc., which are called "mineral facings."

In its application to green sand molds, graphite and blackings are usually dusted on and then slicked off with a tool, or rubbed on with the hand and the excess blown away. Sometimes it is applied in careful work with a fine brush, care being taken not to disturb the sand surface.

For dry sand molding graphite washes are applied. Liquid adhesives of some sort, such as molasses, glutrin or goulac are used. The latter two are by-products resulting from working up the waste liquor from paper pulp mills. The wash usually contains fire clay. The viscous mixture is applied with swabs or brushes.

The best results in foundry facing work are obtained when high grade flake graphite is used. This material may be considerably diluted and yet be better than the poorer varieties of graphite. Some ingredients in a facing other than graphite are placed there for a purpose depending largely on the nature of the work required to be done by the facing. In a number of cases, the added material is almost as essential as the graphite itself. Soapstone is added to facings to improve their properties. Coke, anthracite and even bituminous coal are often ground up with the graphite to cheapen the mixture. Large quantities of amorphous graphite too poor in quality to be used for other purposes, find extensive application in foundry facings. The preparation of proper specifications based upon reliable tests is one of the urgent problems of the foundry.

CHAPTER IX

MISCELLANEOUS USES OF GRAPHITE

AMONG the miscellaneous uses in which graphite finds employment are its use in electrotyping, stove polishes, boiler graphite, in powder manufacture and a large number of industrial applications. While these uses do not consume a great tonnage, they are of considerable importance.

Very finely powdered graphite is used for two purposes in electrotyping. The forms, after being made up, are dusted over with graphite, placed in the machine and highly polished. This allows clean and sharp stripping of the type from the wax mold. In its second use, the wax mold with the impression of the original is then dusted with graphite which spreads freely and smoothly over the whole surface and into the fine interstices of the mold. The wax form is then polished and is ready for immersion in the electroplating bath.

Natural amorphous, flake and Ceylon graphite are all used for the above purpose. In practically all cases only the purest and best grades are used to insure a uniformly polished and conducting surface. This allows good, clean electroplating with true conformity to all details of the mold.

The use of graphite as a conducting coating for forms was proposed by Wood in 1873. In consequence of its unctuous character, graphite adheres better to forms than the various metallic powders which have been suggested as substitutes. A correctly graphitized surface should show a lustrous metallic black appearance. Great care is taken to leave no portion of the form untouched by the brush with which the graphite is applied. On wood and plaster molds

which are saturated with stearin, better results are obtained by the use of pastes of graphite and water.

In large electrotyping establishments the graphite is applied mechanically. A number of machines, some of which are relatively complicated, are employed for this purpose.

Amorphous natural graphites are usually employed in stove polishes. They are worked up into the form of a paste, a cream, a cake, powder or liquid with the addition of a clay, resin, asphaltum or soap binder in the case of the solid polishes and of a gasoline or water vehicle for the liquid varieties.

Mexican and Corean graphite are quite suitable for this application. Carbon black is often added to intensify the color. In all cases, the graphite is first ground to an impalpable powder. In the case of cake polishes, the graphite and clay are first molded or cast into the desired shapes and then baked. The commercial formulae for the various types of polishes are the manufacturing secrets of the individual makers. They vary widely; usually they are a very cheap product.

The use of graphite for preventing scale in boilers has often been advocated. The action of graphite in the elimination of boiler scale is purely mechanical. It is not affected in any degree by the alkalinity or acidity of the boiler feed water or by the temperature. Small particles of graphite work their way through the fissures or cracks in old scale. They gradually penetrate between the scale and the metal, thus loosening the former so it may be readily removed. If the use of graphite is adopted when a boiler is first put into operation, any great accumulation of hard scale may be effectively prevented. The particles become incorporated with the scale as it forms, thus rendering it soft and friable and easily removed.

The variety of graphite usually recommended is very finely ground flake, although the other forms have been used.

The amount of graphite usually recommended is a quarter pound per 50 H.P. It is introduced into the boiler by mix-

ing it with hot water and feeding through the pump suction after blowing down. For locomotives about a pound of graphite per day is considered sufficient for ordinary engines. It is placed directly into the water tank.

Graphite is employed for giving a protective finish to powder grains in order to prevent their being damaged by moisture. It is also used as a polishing material for shot.

Graphite is employed in engine packing, hard rubber compositions, cord and twine manufacture, hat polishing and in the manufacture of cordage, ropes and cables. It also finds application in various types of washers and packing, particularly for piston type machines. Mixed with lead, it forms one of the most suitable high pressure corrosion resistant packings we have.

It is sometimes used in connection with smokeless powder for the purpose of avoiding difference of potential between the grains with subsequent danger of sparking. It is often employed as a filler in fertilizers to coat the particles, thus preventing the absorption of moisture and eliminating caking.

What are known as graphite slabs are used in flattening window glass. These must not be sensitive to sudden changes of temperature and at the same time have great mechanical strength. They are satisfactorily made¹ from a coarse grain material but are surfaced with finer material. A common mixture is 1 to 2 parts of fire clay, 1 to 2 parts of grog, graphite 2 to 1 part. The above materials are mixed dry, screened and pugged to a stiff paste. The material is allowed to age for a few days, again pugged, and aged until needed for use. The slabs are molded in a wooden frame, the working surface being made with fine clay. The latter is usually placed in the bottom of the mold. Filling is continued with coarse material. The slabs are then dried, baked and polished successively with wet sand, finely ground grog and pumice stone or talc.

Graphite is sometimes added to the mix in making mag-

¹ A. B. Searle, Refractory Materials, p. 274.

nesia brick, to increase the facility with which the material may be molded, as well as increasing the heat conductivity of the mass.

The use of graphite in electrodes, in brushes, and in dry batteries will be discussed separately under these specific headings elsewhere in this volume.

CHAPTER X

CARBON BLACK

CONSIDERABLE confusion exists in the use of the terms lampblack and carbon black. In the American trade lampblack is generally understood to be a soot formed by the smudge process. Oil, coal, tar, resin or some solid or liquid carbonaceous substance is burned in an insufficient quantity of air. Carbon black, on the other hand, refers to a product resulting from the incomplete combustion of gas and is deposited by actual contact of the flame on a metallic surface. Lampblack is of a very soft, flocculent nature, whereas carbon black is hard and brilliant. G. C. Lewis is of the belief that lampblack and carbon black differ structurally in that lampblack is amorphous and carbon black is mainly crystalline with a certain percentage of amorphous particles blended in with it. He finds some support for his theory in the X-ray work of G. L. Clark.

Carbon black is often referred to as gas black, natural gas black, ebony black, jet black, hydrocarbon black, satin gloss black and silicate of carbon. It is produced by one of the following methods: (1) Formation by direct contact of a flame upon a depositing surface, usually of metal. (2) Production by heating carbonaceous vapors or gases to a decomposition temperature by external heating with or without air in the forming chamber. This method is usually termed cracking or thermal decomposition. It produces a soft black not unlike lampblack, sometimes greyish and semi-graphitic.

To certain manufacturers of printing ink it was known that the carbon made by burning artificial gas in a limited quantity of air gave the ink a very glossy and intense black. The first factory in which carbon black was successfully made

on a commercial scale from natural gas was erected at New Cumberland, W. Va., in the year 1872.

The first actual use of natural gas for light in the United States occurred in Fredonia, N. Y., in 1826.

In the plant at New Cumberland the gas from the gas holder passed through pipes to gas jets arranged in the same horizontal plane beneath slabs of soapstone that were pierced with a number of orifices to permit the passage of excess smoke and the waste gases. The slabs were covered by a dome or roof that was provided with a damper for controlling the ventilation. Transverse horizontal scrapers were mounted below the slabs. These scrapers from time to time removed the deposited carbon black. The resulting product sold for \$2.50 per pound but did not possess all the properties of the product made from artificial gas. This plant was built of wood and was destroyed by fire after running a short time.

The next innovation in the carbon black industry was the use of a traveling car which hung from rails running parallel with the bench. This car carried a scraper and a shallow frame to which were attached on each side two deep receptacles of sheet iron that could be detached and emptied. Results soon showed that the dome was superfluous, that cast iron was better than soapstone as a depositing surface, and that there was practically no beneficial effect from artificial cooling.

Peter Neff built a plant at Gambier, Ohio, and through competition the price of carbon black was greatly reduced.

In 1883 a considerable advance was made in the industry when L. Martin & Co. became interested in a small plant at Fosters Mills, Pa. Here five plates 24 feet in diameter, cast in segments, were supported by a central mast rotating with them upon bronze bedplates. Beneath these plates were fixed stationary burners of parallel, horizontal, $1\frac{1}{4}$ " pipe. At this time carbon black could be purchased for 31 cents per pound.

In the same year A. R. Blood devised a method using a

small disk or plate about 3 feet in diameter as the depositing surface; and E. R. Blood began making carbon black by the roller process, using a burner with a small hole in the tip that gave a round flame.

In 1892 L. J. McNutt procured a patent on the channel system of making carbon black. A factory was constructed at Gallagher, Pa.

At this time in the industry an attempt was made to manufacture carbon black from petroleum by evaporating and burning the vapors through gas burners. The resulting product, however, contained hard particles of carbon similar to coke, which limited its utilization.

In 1913 G. Fernekes obtained a patent on a process for making carbon black by subjecting gas to a temperature which dissociates it into carbon and hydrogen. The decomposing chamber was heated by electric coils. This process is not used commercially.

A patent was issued to R. H. Brownlee and R. H. Uhlinger in 1916 for making carbon black and hydrogen from a hydrocarbon decomposed by burning in contact with a highly heated refractory material within an inclosed chamber, at a pressure in excess of atmospheric pressure.

There are four different processes of manufacturing carbon black from natural gas. In comparison, practically all other sources or raw materials are commercially unimportant. The four processes are the channel system, the small rotating disk, the roller or rotating cylinder, and the large plate process. These methods differ mainly in the size and shape of the surface upon which the black is collected and the rate of travel of the moving device. There are between 60 and 70 carbon black plants in the country. Fully 80% of the carbon black manufactured today is made by the channel process. Classified according to the quantity of carbon black produced, the order becomes: (1) the channel operation; (2) the small rotating disk; (3) the large plate, and (4) the roller process.

Long before arrival at a channel process plant on a clear

day, large dark clouds at a distance indicate the plant location. On arriving, a series of long, low sheet iron buildings is seen. They vary from 80 to 115 ft. long and about 10 ft. wide for a single system and 18 to 20 ft. wide for a double system or set of channels. The buildings are only about 10 ft. high at the apex of the roof and 8 or 9 ft. at the eaves. They are made of 24 gauge sheet iron held by wire to a steel frame made of $1\frac{1}{4}$ " by $1\frac{1}{4}$ " by $\frac{1}{4}$ " angle iron. The ridge pieces of the building do not extend the entire length, as spaces are left to allow the escape of the gases of combustion. The ridge pieces are flexibly attached so that the spaces can be changed and the drafts regulated. Chimneys are provided in the design of some of the plants. Along the bottom of the buildings are slits or slide doors for controlling the air supply. They are usually adjusted to meet the various conditions of the weather. A door at each end and one or two doors on each side furnish access to the interior. In operation, clouds of distinctly reddish-brown smoke slowly rise from the outlets at the top of the building. These clouds consist mainly of water vapor, carbon dioxide and probably some nitrous fumes. They contain surprisingly little carbon black and not nearly enough to pay for the cost of collection.

An inspection of the interior shows a series of iron channels about 6" wide and 5 ft. from the ground. These are moving very slowly and ceaselessly backwards and forwards day and night, and emitting the peculiarly shrill creaking sounds of metal in motion that has not been too well lubricated. With the intense heat it hardly pays to lubricate the system, as no one seems to mind these continual grinding and creaking noises to which they become as accustomed as city dwellers to the noise of subway trains and traffic.

Under these slowly moving channels are long rows of burner pipes with gas flames playing on the channels. About every 4 ft. apart hoppers are provided to receive the carbon black impinged on the channels, the black being removed by iron scrapers. The hoppers deliver the black to

spiral conveyors which feed to pipes all leading to a common center.

The channels themselves are made of mild steel 6 to 8" wide and weighing about $12\frac{1}{4}$ lbs. per running foot. They hang from trucks that run on overhead rails. Standard $1\frac{1}{4}$ " pipe resting either on concrete piers or upon the gas distributing pipes support the channels, trucks, rails and other accessories. Uprights are spaced approximately 4 ft. apart. At the top of each upright is a small cast iron rail chair. These rails weigh 5 to 7 lbs. per foot. Running on the rails are 10" double gudgeon truck wheels whose posi-



FIG. 19.—A CHANNEL PLANT IN PROCESS OF CONSTRUCTION
(Courtesy Bureau of Mines)

tions can be regulated. Attached to the angle irons on both sides of the truck wheel are transverse channel beams weighing $6\frac{1}{2}$ lbs. per foot. To these beams the channels upon which the carbon black is deposited are bolted. Each trestle is about 6 ft. wide and is termed a table. Most plants have 8 rows of channels on each trestle. Fig. 19 shows an installation of this type under construction. The channels are bolted together in lengths as great as 100 ft. and the trestle is 10 to 15 ft. longer to allow for the oscillations of the table.

Below the channels are the collecting hoppers. Each hopper is made of three parts, — the crown, the body, and the base. The crown is supported on the trestle by $1\frac{1}{2}$ " by $1\frac{1}{2}$ " by $\frac{1}{4}$ " angle irons on each side and sits loosely in the body which is about 6 ft. in width in the upper portion, tapering down to about 10" at the bottom. The base is about 15" high and carries a conveyor pipe at the bottom.

Scrapers are of two types: those which operate continuously and those which are in direct contact with the channels only when the table is moving in one direction. A more uniform grade of black is obtained by the latter method. The scrapers are of $1/16$ " steel, $1\frac{1}{2}$ " wide and 8" to 11" in length. They have two blades attached to a 20" arm carrying a loop on which a weight is suspended only if the scrapers remove the deposited black continuously. Intermittent scrapers are tripped out automatically in one direction by cams and levers. Most plants have side scrapers for removing the deposits from the sides of the channels. A table having 8 channels would have 9 side scrapers. The side scrapers are made of $\frac{1}{4}$ " strap iron.

The conveyors for removing the deposited black from the hoppers are of the spiral or screw type. They are usually made of galvanized iron and are 7" to 8" in diameter. The helical screws are usually made at the carbon black plant on a simple tinsmith's machine, which cuts disks of sheet iron slightly less than 7" in diameter and bores a small hole in the center for the shaft. The shaft is ordinarily standard 1" pipe supported over 8 ft. by cast iron spider bearings or conveyor hubs. At the discharge end of each conveyor there is an overflow tee made of a short pipe connected to the conveyor. The tees are usually capped. Below the tee and connected at right angles to the conveyor is the outlet pipe delivering the collected black to the main conveyor.

The space between the hoppers constitutes one section of the trestle. The burners are placed here. The burners are parallel to and about 3" to 4" below the channels. Each burner holds 8 to 10 lava tips. The lava tips are made of

selected steatite or soapstone. The rock is easily machined in its green condition to any desired form. After calcining to about 2,000° F., it is mechanically hard and strong. The most common type of tip burns 4 to 14 cu. ft. of gas per hour. A typical lava tip has a slot 0.2" deep and 0.034" wide.

It will be noticed in some plants that the edges of the gas flames from the tips curl right over the channels. Close observation will show tinges of red and yellow near the channels streaked with black. In other plants the burner pipes might be set lower or further away from the channels, allowing more of the tip of the flame to come in contact with the metal. Various grades of black are made by changing the size of the burner tip, the compression of the gas, the height of the flame, the area of the channels as well as their velocity of motion.

Mechanical details for reversing the direction of the channels are quite similar to those used in other industrial operations requiring direction reversal.

A large amount of work has been done by the L. Martin Company on the study of flames. G. C. Lewis, Chamberlin and Thrun made a number of studies on flame pulsation and vibration. It was found that flame vibration conformed to simple harmonic motion.

When a gas under a pressure burns in air, oxidation takes place around the whole mantle of the flame, forming an invisible hot outer zone of carbon dioxide. As the unburned gas rises within this mantle, air diffuses through the carbon dioxide layer and some oxidation takes place. Some of the hydrocarbons are broken down forming carbon as a result of the pressure oxidation. The incandescent solid carbon particles give the yellow color to the luminous zones. Methane, ethane, carbon dioxide, carbon monoxide, hydrogen, nitrogen and water vapor exist in this luminous zone. Directly at the top edge of the luminous zone is the non-luminous one. Here the oxygen has been consumed but the change from luminosity to non-luminosity is due to the re-

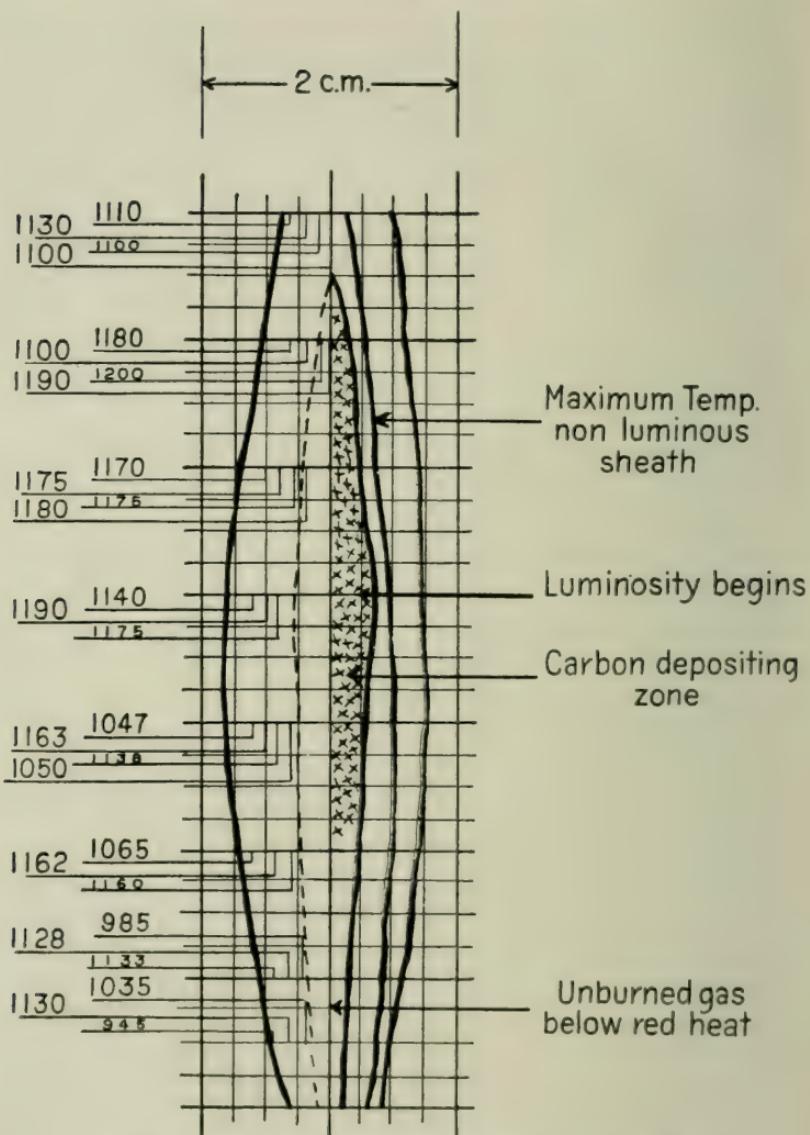


FIG. 20. -- TEMPERATURES OF NATURAL GAS FLAME

duction of the carbon dioxide by the carbon. There is apparently no hydrocarbon decomposition in this zone to carbon.

Figure 20 shows a diagram, due to the courtesy of Mr.

G. C. Lewis, of the various temperatures of a natural gas flame. The variation is from $1,000^{\circ}$ to $1,200^{\circ}$ C. The temperatures were obtained pyrometrically in a very careful manner.

The thickness of the flames remains constant at different rates of gas flow. When the slot width of the tip is increased by 66%, a thickness increase of only 3.7% is obtained. Distance from the tip at which carbon black begins to form is the same for a wide range of flow rates.

After delivery of the collected black to a central point, the grit, scale and hard particles are removed by bolting machines. These vary greatly in design, but usually all carry fibre brushes which direct the black through the silk bolting cloth. The material not passing through the screen is discarded periodically. The packing machines used for carbon black are similar to those employed in sugar refineries. An auger inside of a tight sheet steel tube presses the black into a large paper bag. The machines are gauged to pack uniform amounts per bag, usually $12\frac{1}{2}$ lbs. or a quarter of a barrel. Bags for export often contain 15 lbs.

Four packing machines are the usual equipment for a 60 barrel plant. The inner shaft of a packer rotates slowly in order to effect the proper separation of the carbon black from the air in which it floats or which it holds mechanically. The separation of the air from the black as far as commercially possible constitutes the chief problem of packing. The bags are tied and, in most plants, slightly compressed, the sides flattened out to facilitate transportation, and a second paper bag placed over the package. Carbon black for export is usually packed in wooden boxes 3 by 3 by 2 ft., each holding from 12 to 15 bags.

The small rotating disk process. The small rotating disk process was invented by A. R. Blood in 1883. The depositing surface is shown in Fig. 21. This disk is made of cast iron ranging in diameter from 3 to $3\frac{1}{2}$ ft. and has approximately a 50-inch face. The burner tips made of soapstone are set in a circular piece of standard $\frac{3}{4}$ " pipe.

This burner ring, usually being about 28" in diameter, carries from 18 to 24 tips. The carbon scraper is of the continuous variety. It is set over a hopper radial with the disk. A driving gear is bolted on the disk and its meshing pinion attached to the drive shaft by the use of a set screw. Extraordinary long pinion teeth are used to allow for expansion and contraction of the entire length of the driving shaft. A shaft base sets in the axis upon which the shaft

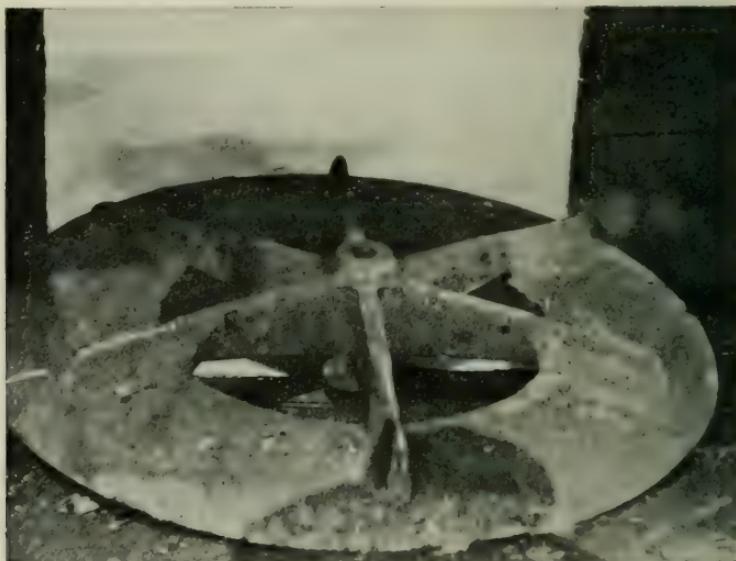


FIG. 21.—CARBON DEPOSITING SURFACE IN ROTATING DISK PROCESS
(Courtesy Bureau of Mines)

rotates. It thus supports the driving shaft and acts as a guide. It also stabilizes the pipe which rests on a concrete base and carries the weight of the disk. The speed of the disk is 4 R.P.M.

The depositing surfaces are arranged in rows of 21 disks with 2 or 4 rows per building. Conveyors are provided for each pair of rows. Each row is driven by a separate drive shaft running the entire length of the building.

Delivery of the carbon black from the building is the same as in the channel process. The yield and quality of

the black are approximately the same as that made by the channel method.

The Cabot process. The plate system was invented by G. L. Cabot in 1892. One of its modifications uses stationary plates 24 ft. in diameter. Revolving scrapers and burners are located underneath the plates. The other modification employs stationary scrapers and burners and rotating plates. The first arrangement is the more widely used.

The iron plates are made of 48 segments, 16 in the inner row and 32 in the outer. Perforations in the plates act as ventilator holes. These afford a means of maintaining a draft and at the same time allow the products of combustion to escape. The plate is supported by guys screwed into a cap which is shaped like a truncated cone. The cap rests upon the top of a hollow vertical shaft, termed the mast. The joint is made gas tight with asbestos packing. A 26 ft. diameter sheet iron building surrounds the plate. The roofs of the building are made partly of triangular pieces of sheet iron and partly of four-sided sheets of corrugated iron extending about $2/3$ of the distance up the 16-ft. mast. There is thus left an open space about 8 ft. in diameter which acts as a vent.

A vertical pipe concentric with the mast is fixed in a bed plate carried on steel balls in grooves. A bottom casting fixed to this pipe carries the circular iron angles by means of pipe struts. Horizontal holes accommodate horizontal guy rods which are connected at their inner ends to an octagonal plate rotating with the burners and scrapers around the central stationary mast. The burners fit in a grid iron of pipe lying on a circular bar iron bolted to the inner vertical face of the angle ring. The gas is fed underneath the plates from burners the ring of which revolves around the mast.

The gas line from the regulators connects to the mast at the bottom. The mast is closed above by a cap from which hang the oblique guys carrying the collecting plate. Slightly below the scraper box are $3/4"$ perforations that admit the gas into the gas box. Two $1\frac{1}{2}"$ pipes are connected to the

INDUSTRIAL CARBON

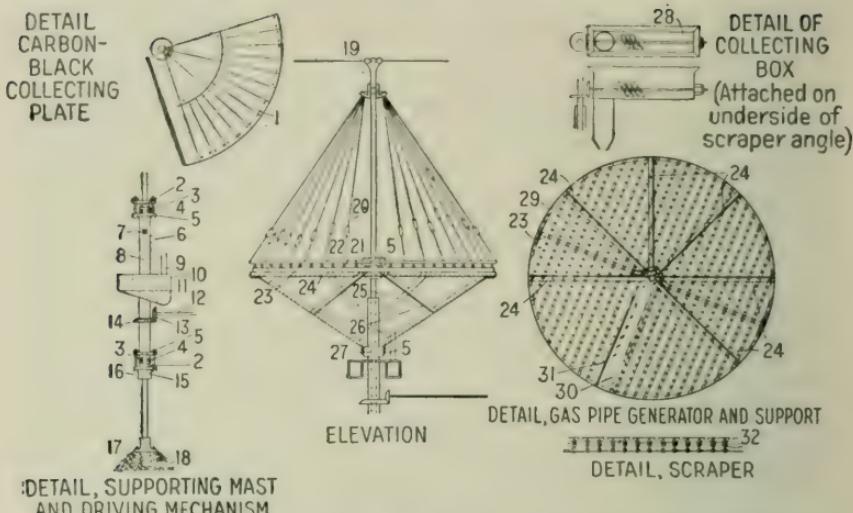


FIG. 22 — DETAILS OF THE PLATE OR CABOT PROCESS OF MAKING CARBON BLACK

1. Hole for attaching guys. 2. Stuffing box and gland. 3. Packing. 4. Pipe plug. 5. Collar and set screw. 6. Tap for gas. 7. Inner shaft plug. 8. Openings, gas from inner tube to outer tube. 9. Carbon black. 10. Revolving cover plate. 11. Screw conveyor. 12. Driving shaft. 13. Pinion. 14. Gear. 15. Ball bearings. 16. Loose collar. 17. Concrete base. 18. Gas intake. 19. Cable support from one unit to other unit and to ground. 20. Guy wires or rods with tightening buckles. 21. $1\frac{1}{4}$ inch gas pipes. 22. Cast iron plates. 23. 4-inch gas pipe. 24. Angle irons. 25. Gas. 26. Angle iron supports. 27. Stud bolt. 28. Screw or paddle conveyor. 29. Supporting and tie-up angles. 30. Collecting box. 31. Angle scraper. 32. Attached rods and springs.

gas box. These pipes feed a 4" main in which are screwed the $1\frac{1}{2}$ " burner pipes extending beneath the surface of the deposition plate. Each 4" pipe feeds over fifty $1\frac{1}{4}$ " pipes set at equal intervals and extending to the periphery of the circular depositing plate. These pipes carry the lava tips. There are 1,265 tips under the entire plate. The burner speed is 8 R.P.M.

The black is removed from the plates by scrapers placed radially on the mast. Collecting boxes below deliver to screw conveyors. The conveying arrangement is quite similar to that in the other types of plants.

The amount of power used in the Cabot process is surprisingly small because all of the machinery in the plant moves so slowly. A 35 horsepower gas engine operates 22 plates and at the same time furnishes power for the conveyors, packing and bolting machinery.

The construction and set up of the plates and burners will be better understood by reference to Fig. 22 showing the mechanical details. A better idea as to what the plant looks



FIG. 23.—CARBON BLACK FACTORY IN WEST VIRGINIA USING THE PLATE PROCESS
(Courtesy Bureau of Mines)

like will be had from Fig. 23 showing a factory in West Virginia using the Cabot process.

The roller or rotating cylinder process. This process was first used by E. R. Blood in 1883. It originally proved unprofitable because of the small yield. Later when a market for the product, which possesses valuable properties, had been created, the details of operation were improved. At the present time roller process black is the highest grade of carbon black, despite its inferior color. It is utilized chiefly in making lithographic and embossing inks and printing ink or half-tone engravings.

The details for the roller process will be easily understood by referring to Fig. 24. The gas burners are located directly underneath a rotating cylinder. A $1\frac{3}{4}$ " pipe leads the gas to each set of rollers. The burner pipe

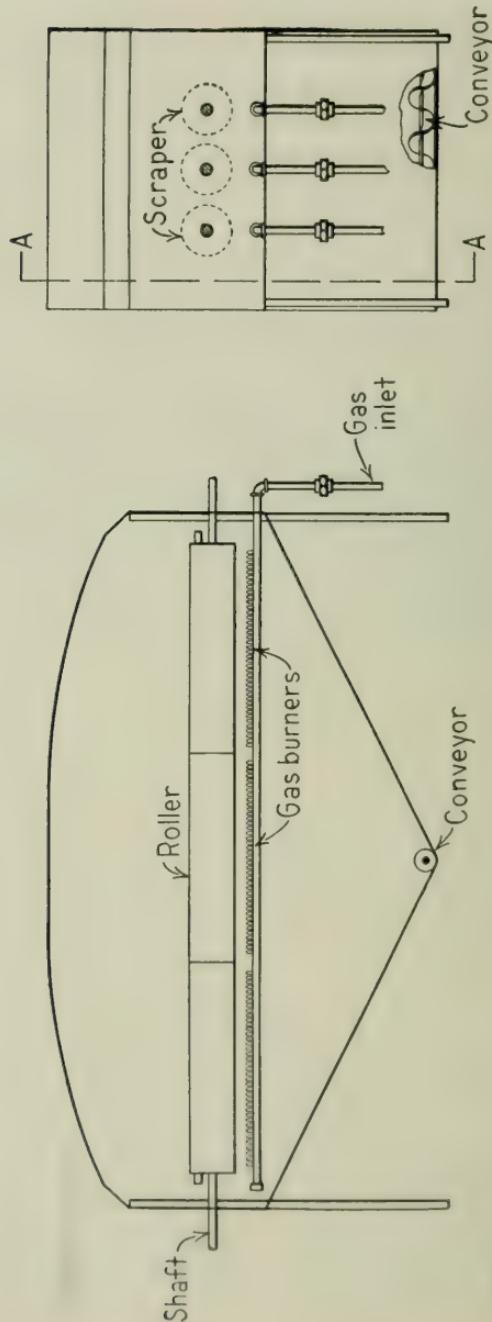


FIG. 24.—DETAILS OF ROLLER OR ROTATING DISK CYLINDER PROCESS

carrying the lava tips is 3" to 5" below the rollers. The lava tips themselves are round and produce a cylindrical flame as the result of a round rather than a fishtail opening. The rollers are 3 to 8 ft. in length, having a spider bearing for a $1\frac{1}{2}$ " shaft. When made of cast iron $8\frac{1}{2}$ " outside diameter with $7/16$ " walls, they weigh approximately 100 lbs. The roller surfaces are machined. Some operators

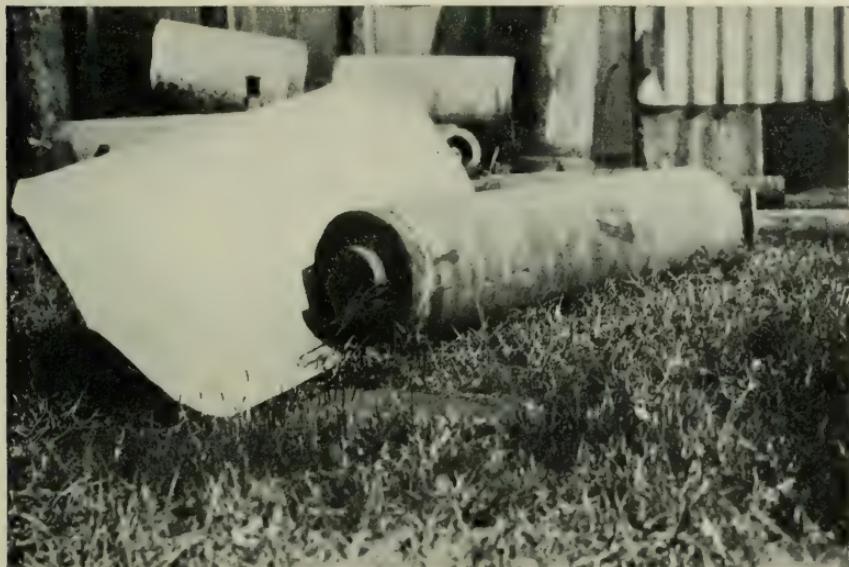


FIG. 25.—CYLINDER UPON WHICH CARBON BLACK IS DEPOSITED IN
ROLLER SYSTEM
(Courtesy Bureau of Mines)

replace these cast rollers with extra heavy well casing pipes in 8 or 9 ft. lengths.

Scrapers are placed at or near the top of the rollers running the entire length. They are of the continuous type, being in direct contact.

Removable sheet iron hoods cover the rollers and protect them from drafts. Apertures are provided so that ventilation may be controlled. Trough-shaped collecting hoppers are located below the rollers. At their bottoms

they carry screw conveyors delivering the black to central points. An angle iron frame supports the hood, the hopper and the conveyors. Each hood covers 9 rollers, there being 3 rollers on each shaft. Each building ordinarily contains 2 rows of hoods and scrapers, the shafting running the entire length of the building. Slits or slide doors in the building help regulate the draft. A typical building has 196 to 288 rollers, 10,000 lava tips, with 24 to 32 hoods. The buildings are from 65 to 100 ft. long and 25 to 35 ft. wide.

Large numbers of gears are required to actuate carbon black plant machinery. The temperature changes occurring in the plant give rise to a special problem which is solved by using gear pinions with facial dimensions 4 or 5 times those of the gears which they mesh. This is done so that the gears and pinions will mesh at all times, even though there be sudden or large contractions or expansions in the shaft.

A number of patents have been obtained by various inventors for the production of carbon black from natural gas by cracking or thermal decomposition. The carbon black produced by this procedure is grayish in color, possessing a high specific gravity. The black contained hard particles, but experimental work has corrected this condition. The first commercial products produced were almost unsalable except for the manufacture of very cheap paints. The thermal decomposition method has possibilities of giving high yields of black but the product is of an inferior quality and in most cases it is not considered for use by the usual consumers of carbon black.

COMPARISON OF DIFFERENT PROCESSES

The channel, rotating disk, and large plate methods give carbon black yields per unit volume of gas which are approximately the same. The roller system produces considerably lower yields but the resulting product has special applications. The carbon black yields in the first three processes mentioned vary from figures as low as .78 lbs. carbon

black per 1,000 cu. ft. of gas to as high as 1.4 lbs. in some plants. The average, however, is between 1 and 1.1 lbs. carbon black per 1,000 cu. ft. of gas.

The channel system plants can be built almost entirely from standard structural steel shapes with the resultant cost of construction less than that of any other type. The large plate method requires special large castings entailing a high initial construction cost. The roller process also requires special castings but the plants are more flexible than those of the channel process in that while parts may be out of order, the remaining sections of the plant may operate, and it is not necessary, as in the channel plant, to shut down the whole building for repairs. The roller system requires the largest depositing surface per lb. of black made. Only a relatively small amount of black is made by the roller process. The depositing surfaces in channel plants vary from as low as 3.7 to approximately 5 sq. ft. per lb. of carbon black. The small disk is of the order of 3 to 4 sq. ft., the large plate, 6 to 7, and the roller 9 to 10.

The yield of carbon black is affected first by the quality of the natural gas, some gas being lean and others rich; by the design of the plant, its type, the weather conditions, the gas pressure, the presence of salt water and oil in the gas, the kind of lava tip used, the distance of the top of the lava tip to the depositing surface, the method of admitting air, and the rate of movement of the collecting surface. Most of these factors are determined empirically only after the plant is in operation.

A typical Louisiana plant is shown in Fig. 26. Weather conditions markedly affect this type of plant. Wind cuts down the yield by causing the flame to flicker. Moist weather or light rains have little effect, but heavy rains tend to lower yields and decrease quality. Many times the suggestion has been made of water cooling the depositing surface as a means of lowering the surface temperature and thus increasing the relative efficiency of a process. Even a slight acquaintance with the principles of heat transfer will

show that a surface on which carbon black is deposited is a good insulator and relatively resistant to the flow of heat. Commercial experience has shown that in the large, no beneficial results are obtained by cooling the depositing surface.

Flame temperatures are exceedingly important in carbon black plants, since the black does not separate with a low temperature flame but on the contrary only at a relatively high temperature. If the flame be too cold, the black



FIG. 26.—A LOUISIANA CARBON BLACK PLANT IN OPERATION

(Courtesy Bureau of Mines)

will not be decomposed completely, or if it be too hot, too much carbon will be burned. A depositing surface that is too hot collects less carbon black than a cold one, but a too cold surface chills the flame and less carbon is deposited. The temperature of the channels in the present day process is about 500° C.

It is believed from the results of chemical studies that a methane flame first oxidizes to methyl alcohol then most probably to formaldehyde, formic acid and ketones before the general break down into carbon dioxide and monoxide and, according to the amount of air, water vapor, nitrogen and some little cyanogen. A methane flame will not burn

in less than 15.6% oxygen. Only in the inner part of the flame where there is low oxygen supply but enough heat to break up the methane will carbon black be produced. The percentage of carbon to be had by the incomplete combustion of methane is low. Gases rich in ethane and the higher homologs give greater yields of carbon. Bone, in his experiments on the explosive decomposition of hydrocarbons, noted that the decomposition of methane was a surface effect producing a hard, gritty carbon, but that the decomposition of ethane, ethylene and similar gases took place throughout the whole mass and gave a soft carbon.

Practically every carbon black plant has gasoline absorbers in which the gas is passed, either mineral or seal oil which strips it of its gasoline content. Stripping the gas has no appreciable effect on either the quantity or the quality of the black produced. The gasoline recovery from natural gas is in many cases a large source of revenue.

The presence of salt water and considerable sulphur in the gas is often quite disadvantageous. The salt crystallizes and the sulphur compounds accumulate on the lava tips partially or wholly blocking the openings so that the flames are interfered with.

The gas pressure will affect not only the quality but also the quantity of the black produced. The pressure on the distributing lines to burners varies from .2 to 1.5 inches of water. With excessive pressures the yield of black is low.

The factors which determine the location and construction of a carbon black plant are: (1) Shipping possibilities, to be determined by the distance of the plant from a railroad or a navigable stream. (2) The individual state laws in reference to natural gas and oil resources. (3) The depth of gas wells and the thickness of the gas-bearing strata. (4) The gas pressure and its gasoline content. (5) The type of gas,— whether of the casing head variety or the dry gas type. (6) The amount of proved territory, the history of the field, and its drilling practice. (7) The location of the field in regard to large gas consuming centers and its

distance from trunk line pipes for gas transportation. (8) The open flow capacity of the wells and the available quantity of gas and its richness in respect to the possible amount of carbon black to be obtained per unit volume of the gas.

Carbon black plants are situated in isolated districts where there are no pipe lines and gas is cheap. It may, however, be uneconomic to operate a plant because the plant location entailed an unusual amount of transportation difficulties.

There are many hazards in gas supply. Some of them are almost intangible. Geological surveys of the field may give some idea of its possibilities. If a newly developed field becomes extensive and prolific, pipe lines are usually constructed to it. At this point the price of gas will gradually increase and as the production and rock pressure decline and compressors are applied to the gas, it will increase in value so that the manufacture of carbon black will become prohibitive on an economic basis. As an example, in some localities of West Virginia gas formerly sold for 2.5 cents per 1,000 cu. ft. The introduction of compression plants and transportation lines caused a price increase to 8 to 20 cents. Even though the carbon black manufacturers own the wells, it is more profitable to sell the gas than to use it for carbon black manufacture.

Often the gasoline content of a natural gas may be so large that the operator can pay a high price for the gas and still find the manufacture of carbon black profitable. At the greater number of the plants the gas is stripped of gasoline by an absorption process, ordinarily employing some form of charcoal or synthetic gas-adsorbing carbons.

Carbon black was first manufactured from artificial gas. The product is very glossy and has intense color, and makes a high priced printing ink. Were it not for the prohibitive cost of the raw material, carbon black could be manufactured from artificial, illuminating, blast furnace, producer, by-product, or coke oven gas. There are a number of patented processes in which a black known as acetylene black

is made by exploding mixtures of acetylene and air under pressures of 50 to 100 lbs. per sq. in. It is stated that the acetylene is not merely oxidized but is dissociated. Acetylene is made from refuse calcium carbide of non-commercial grades either too finely ground or too low in carbide content. The product has an inferior color and strength when compared with natural gas black, although it is preferred for some uses because of its inherent bluish tinge. It is soft like lampblack, with exceptionally high oil adsorption properties. Yields of 10 lbs. of black per 1,000 cu. ft. of acetylene have been claimed. Blacks made by burning acetylene are of better color than those made by explosion.

The cost of construction of a carbon black plant before the war was approximately \$1,000 per 50-lb. barrel per day capacity. The figure now has increased to nearer \$3,000 a barrel for channel plants. The cost of construction of a rotating disk process plant is slightly greater. Labor costs in carbon black plants are low, inasmuch as the most of the work is automatically performed by machinery. The daily production per man in channel plants varies from 250 lbs. in the smaller plants to as high as 750 lbs. in the larger ones. In roller process plants this figure may be as low as 100 lbs. per man per day; in rotating disk and plate plants, of the order of 400 to 500 lbs. per day. The cost of operation, not including the cost of the gas, varies from \$1.50 to \$3.50 per 100 lbs. of carbon black produced. This takes into account labor cost, sacking, resacking, depreciation, supplies, and repair and maintenance. The cost of gas varies from 3 to 8 cents per 1,000 cu. ft. at the present time and the price is steadily increasing. Some special high-grade carbon blacks cost nearly 50 cents per lb. to produce. These are specially used for lacquers. Most of the companies charge off 10% a year depreciation to cover the hazards in the supply of gas.

The utilization of low pressure gas in the manufacture of carbon black and of gas escaping into the air, of natural gasoline plants, gas in distinctly isolated districts, and gas

in fields that have been abandoned by other gas companies because of low pressure, is in reality often a conservation measure. Its consumption by the manufacturer of carbon black is decidedly preferable to the practice of letting gas go to waste in the air or to plugging the wells improperly so that the gas sands can be damaged by flooding with water.

Thermal decomposition offers an interesting field to research as a possible means of increasing the relative efficiency of the carbon black industry, although at the present time there is no more efficient process known than the incomplete combustion of natural gas for making a product which has all the desired properties of carbon black.

The chemical analyses of commercial carbon blacks vary between relatively wide limits, although in all cases the ash content is very low. The fixed carbon and volatile matter may be quite variable. For the sake of completeness, a table of analyses of a number of commercial carbon blacks is included in this chapter.

The uses of carbon black in order of their importance are in the manufacture of the following products: rubber, printing ink, paints and enamels, lacquers, stove polishes, other products such as phonograph records, carbon paper, crayons, typewriter ribbons, black and gray paper, tarpaulins, black leather, book binders' board, marking and stenciling inks, rubber goods, artificial stone and black tile, insulating materials, electric arc carbons, buffering powders, and to a very small extent in case hardening. More than 100 million lbs. per year are used in rubber, from 20 to 25 million in printing inks, approximately 10 million lbs. in paints, about 4 million lbs. in stove polishes and somewhat more than 10 million lbs. for other miscellaneous uses not including 40 to 50 million lbs. annually exported.

For certain purposes, such as phonograph records, medical hard rubber, all soft rubber goods such as footwear, tubing, and heavy truck tires, certain kinds of printer's ink and black paint, it is possible to substitute lampblack for carbon black, but for most purposes these two products are quite

dissimilar in their physical properties and to date have proved unsuitable for substitution.

CARBON BLACK IN RUBBER

Although the carbon black industry owes its early existence to the printing press, its recent growth and present economic status are due to the rubber industry, which in turn is dependent upon the automobile. The most remarkable chapter in the story of carbon black has been its world-wide adoption by the rubber trade during the past decade. Automobile owners of the early days vividly recall how frequently blow outs occurred. After a long search for something which would make tires tougher and more serviceable, the rubber chemist hit upon carbon black. Beginning with one or two of the large American manufactures, the use of carbon black in tire tread stocks spread rapidly throughout the entire rubber industry. Approximately 100,000,000 pounds or more per year are now consumed by the rubber trade. Virtually all tire treads are black.

Carbon black finds its chief use as a filler in rubber because its finely divided state greatly reduces oxidation and increases the tensile strength of the mixture. Carbon black is not considered as indispensable in rubber as in printing ink. In times of high prices it has often been supplanted by zinc oxide or graphite. Zinc oxide, which had early obtained a position as an important filler, became too costly soon after the outbreak of the World War. It was then shown that carbon black could be successfully used as a substitute.

Carbon black as a rubber filler is now used to the extent of 3 to 20%, according to the purpose for which the rubber is required. On a volume basis, carbon black with the specific gravity of 1.8 costs only $1/3$ the price of zinc oxide with the specific gravity of 5.6. In actual practice, however, a greater volume of carbon black is used than of zinc oxide so that the resulting mix contains less rubber per unit volume than the zinc oxide mix.

TABLE III
ANALYSES OF CARBON BLACKS

Brand	Manufacturer	Method of Manufacture	Condition ²	Proxi-	
				Moisture	Volatile Matter
G Elf carbon black	G. L. Cabot	24-ft. plates, large burners, Grantsville, W. Va.	1	2.76	10.49
P N Elf carbon black	G. L. Cabot	3-ft. plates, large burners, Spencer, W. Va.	2 1	2.58	10.79 8.37
New Vulcan carbon black	G. L. Cabot	3-ft. plates, average size lava tips, Grantsville, W. Va.	2 1	3.12	8.59 5.58
Monarch carbon black	G. L. Cabot	Channels, medium size lava tips, Glasgow, W. Va.	2 1	2.34	5.76 6.16
Kalista carbon black	G. L. Cabot	Cylindrical rollers, cylindrical burners, Creston, W. Va.	2 1	5.30	6.31 10.40
Auk carbon black	G. L. Cabot	Channels, medium size lava tips, Glasgow, W. Va.	2 1	2.64	10.98 7.06
Long carbon black	Binney & Smith	Probably cylindrical roller system	2 1	7.13	7.25 13.41
Short carbon black	Binney & Smith	Probably channel or 3-ft. disk.	2 1	3.02	14.44 5.48
Rubber carbon black	Binney & Smith	Probably channel or 3-ft. disk.	2 1	3.02	5.65 5.33
No. 54 carbon black	Binney & Smith	Unknown	2 1 2	2.48 2.74	5.50 8.07 8.27
Sample from a rubber company carbon black	1 2	2.74	7.81 8.03
Triangle carbon black	Eastern Carbon Co.	3-ft. disks, Shrewsbury and Barren Crk, W. Va.	1	2.25	5.60
Bull's-eye carbon black	Eastern Carbon Co.	Unknown	2 1 2	3.56	5.73 11.99 12.43

² 1 denotes sample as received; 2, dried at a temperature of 105° C.

TABLE III — (Continued)
ANALYSES OF CARBON BLACKS

MATE		ULTIMATE					CALORIFIC VALUE		Real Specific Gravity
Fixed Carbon	Ash	Hydro- gen	Carbon	Nitro- gen	Oxy- gen	Sul- phur	Calo- ries	B.T.U.	
86.64	0.11	1.02	91.97	0.02	6.86	0.02	7,578	13,640
89.10	.11	.73	94.58	.02	4.54	.02	7,793	14,027
89.04	.01	1.14	92.20	.07	6.17	.41	7,592	13,666
91.40	.01	.87	94.64	.07	3.99	.42	7,793	14,027	1.74
91.22	.08	1.05	93.63	.05	5.19	.00	7,651	13,772
94.16	.08	.72	96.64	.05	2.51	.00	7,897	14,215	1.78
91.50	.00	.78	92.90	.08	6.22	.02	7,596	13,673
93.69	.00	.53	95.13	.08	4.24	.02	7,778	14,000	1.86
84.16	.14	1.11	87.98	.08	10.68	.01	7,106	12,791
88.87	.15	.55	92.91	.08	6.30	.01	7,504	13,507	1.88
90.30	.00	.86	92.53	.06	6.55	.00	7,570	13,626
92.75	.00	.59	95.04	.06	4.31	.00	7,775	13,995	1.85
79.44	.02	1.32	84.56	.04	14.00	.06	6,817	12,271
85.54	.02	.57	91.05	.04	8.26	.06	7,341	13,214	1.78
91.47	.03	.88	93.50	.04	5.25	.30	7,618	13,712
94.32	.03	.52	96.41	.04	2.69	.31	7,855	14,139	1.80
91.62	.03	1.02	93.82	.02	5.06	.05	7,778	14,000
94.47	.03	.70	96.74	.02	2.46	.05	8,020	14,436	1.81
89.43	.02	.99	92.74	.03	6.20	.02	7,660	13,788
91.71	.02	.73	95.10	.03	4.10	.02	7,855	14,139	1.82
89.42	.03	.78	92.86	.03	6.29	.01	7,635	13,743
91.94	.03	.49	95.48	.03	3.96	.01	7,850	14,130
92.13	.02	.74	94.78	.09	4.37	.00	7,706	13,871
94.25	.02	.50	96.96	.09	2.43	.00	7,883	14,189	1.87
84.40	.05	1.19	88.17	.04	10.54	.01	7,212	12,982
87.52	.05	.82	91.42	.04	7.66	.01	7,478	13,460	1.80

The influence of particle size on specific surface is of great importance in the rubber industry. The apparent surface of barytes very finely ground is approximately 30,500 sq. in. per cu. in., while carbon black has a calculated surface of 1,900,000 sq. in. per cu. in. Theoretically, carbon black, because of its fine state of subdivision, should be an ideal rubber filler.

A simple rubber-sulphur mixture has a tensile strength of 1,150 pounds. By adding an equal weight of zinc oxide, the tensile strength may be increased to 3,400 pounds. But by substituting for the zinc oxide 35% of carbon black, the tensile strength goes up to 4,000 pounds. At the same time the ability of the rubber to store energy, i.e., to take up shocks, becomes almost double that of the zinc oxide mixture. In other words, the carbon black rubber compound is stronger and more resilient, wears longer and is less susceptible to cuts, punctures or abrasion. Incidentally, the black rubber tire is appreciably lighter than a tire made in the old-fashioned way, which is another advantage.

Wiegand³ and Schippel⁴ have investigated the volume increase of compounded rubber under strain, and also the stress-strain curves, and the results indicate generally that the finer the state of subdivision the larger the proportion of inert filler which can be mixed with rubber without resultant loss of tensile strength. In the case of carbon black, apparently up to 40% may be compounded, and the rubber is thus hardened and stiffened without loss of tensile strength. The volume increase at 200% elongation varies from 1.46% in the case of carbon black and 1.76% in the case of lampblack to 13.3% in the case of barytes—zinc oxide apparently behaves somewhat abnormally.

The rubber industry is the shock absorber of the carbon black industry, normally requiring the major portion of the output and able to absorb a larger percentage in times of low prices. The use of carbon black in ink and paint is

³ J. Ind. Eng. Chem., 1921, 13, 118.

⁴ Ibid., 1920, 12, 33.

limited by the conservative growth in the output of these commodities. Although the link between the rubber manufacturers and the carbon black producers is necessarily close, sentiment plays no part in their business relations. When demand exceeds production and prices are high, manufacturers tend toward other materials and zinc oxide is more largely used.

TABLE IV

The Results for Mixings Containing 20 Volumes of Pigment

Pigment	Apparent Surface	Displace- ment of Stress-strain Curve	Volume Total Energy of Resilience at 200% Elongation	Volume Increase %
Carbon black	1,905,000	42	640	1.46
Lampblack	1,524,000	41	480	1.76
Red oxide	152,400	29	355	1.9
Zinc oxide	152,400	25	530	0.8
Whiting	60,900	17	410	4.6
Fossil flour	50,800	14	365	3.5
Barytes	30,480	8	360	13.3

A recommended specification for carbon black to be used in rubber is: moisture, less than 4%; acetone extract, less than .5%; ash, less than .25%; tinting strength, not less than 90% of the standard. In addition, the material should feel as an impalpable powder when rubbed under the fingers and all should pass through a 100 mesh screen. It should contain no grit.

The use of carbon black in rubber compositions is by no means restricted to automobile tires, but has spread to many other articles, such as hose; surgical and mechanical rubber; floor composition; and all products in which resistance to wear is a prime requisite. One recent development is a rubber device now used instead of a shackle bolt upon trucks and pleasure vehicles. Another is a lining for ball mills, where the durability of rubber reinforced by carbon black has been found superior to that of steel.

CHAPTER XI

LAMPBLACK MANUFACTURE

THE industry of making lampblack, in its early stages, was undoubtedly of the crudest character. With the invention of printing and the manufacture of black paints, a demand arose for improved methods of manufacturing lampblack.

Lampblack is, generally speaking, the smoke from an unobstructed hydrocarbon flame, the solid particles being deposited in chambers from the smoke conducted through flues from the furnaces. Various oils, resins and fats have been used for centuries. Until the development of illuminating gas from coal, resin was used very extensively. The general method was to heat the resin in an iron pan by means of a small fire underneath, then ignite it and lead the smoke into tents lined with sheepskin, the sides of the tent being beaten at frequent intervals to knock down the deposit of soot.

The most primitive method of making a soot pigment like lampblack consisted in burning materials such as resins in a container in a closed room. The material was allowed to burn until stifled by its own smoke through lack of oxygen. It is very likely that the principle of restricted air supply was adopted in ignorance. The yields from this method were small, the method itself slow and costly, and the product not entirely satisfactory. The quality of the material was poor, inasmuch as much unconsumed material such as empyreumatic bodies, oils and heavy moist, bad-smelling substances remained in the black.

When better methods were adopted, a plant similar to that shown in Fig. 27 was employed. The collecting chamber was separated from the generating chamber, the

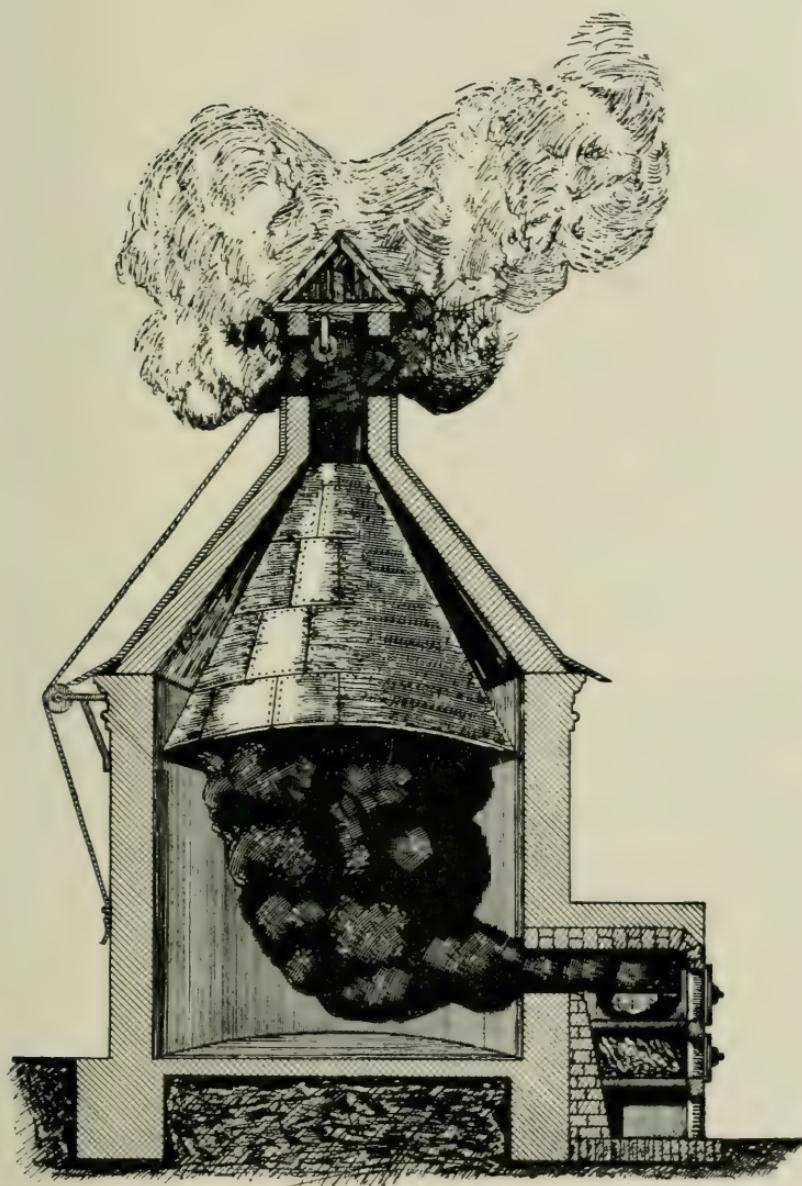


FIG. 27.—AN OLD PLANT FOR LAMPBLACK MANUFACTURE

former being a cylindrical tower with a conical roof. The generator was a small building alongside the tower, in which the raw materials were burned. The black passed through a hole in the wall into the tower. The waste gases passed off at the top of the tower. Deposition of the product was poor and considerable black was carried off mechanically by the waste gases.

The walls of the collecting tower were lined on the inside with sacking to make them rough and to facilitate the adhesion of the soot. When the burning was finished, the black was removed from the walls by lowering a large metal inverted hopper from the roof. This scraped off the black, dropped it to the bottom of the furnace from which it was shovelled up.

There have been many changes in the furnaces and chambers, but by and large, the principle remains the same. A modern plant consists of one or more furnaces burning oil with incomplete combustion. Regulation of suction and blower fans by dampers determines the proper amount of air.

The finer grades of lampblack were made by constructing a series of small chambers, hoods or bonnets, opening into each other, with a furnace at one end. The line terminated in a chimney which created a draft. The smoke passed from chamber to chamber, the heaviest particles depositing in the first of the series and the finest particles in the last. In this way lampblack or soot was graded. This crude method of manufacture was used both in Europe and in the United States until about 1850.

In England, France and Germany, the principal raw materials were tar oils, lard oils and resins. In the United States a considerable quantity of black was made from fish oils, and this manufacture was carried on in Massachusetts. Most of the works were located on Cape Cod, and up until about 1880 there were a number of these small works. The product was known as Cape Cod Black.

There was a considerable quantity of black made in the

United States from resin, and resin dross. The first works of any importance were erected in Baltimore and Cincinnati for the manufacture of what was known as Resin Lampblack. This same kind of black was also made in Troy and Watertown, New York.

Blacks made from fish oil and resin contained a large percentage of impurities. It was necessary that these blacks be calcined to make them suitable for printing ink manufacture.

It was not until coal tar oils (or, specifically, those designated in the trade as "dead," or creosote oils) were commercially available, that there was any distinct improvement in the method of making lampblack. Melting materials like resin and naphthalene so as to get them to flow readily through pipes was not practical, or even to burn these products in bowls or pans to prevent the carrying over of a certain amount of free oil and impurities into the black. By the use of tar oils, however, it was possible to burn in a different way, and a vast improvement was made in the process of producing and collecting the lampblack from tar oil.

The buildings now used for this purpose, both in Europe and in the United States, consist of a brick or stone structure, having at one end a number of furnaces especially constructed for the purpose. These furnaces are connected by large pipes or openings into a series of condensing chambers communicating one with the other. Air is admitted through openings or vents into the furnace in order that the quantity of air may be regulated to the amount of oil burnt, these vents being in the form of registers which can be regulated during the process of the burning of the oil.

In the United States both tar oils and petroleum oils are employed. The oil is conducted through pipes leading into the furnaces, each furnace having a separate supply pipe. The oil passing through these pipes drops upon pans or plates heated to a temperature sufficient to ignite the oil. The smoke is liberated from the flame and passes through the openings into the condensing chambers. In these, the

black falls out of the gas currents. The deposit in the last of the chambers (which is farthest from the furnace and nearest the chimney) is stated to be the finest, and therefore the best quality lampblack. Some authorities dispute this, however, as changed conditions may affect results.

This modern method of making oil lampblack has many advantages over the old methods, for not only can the quantity of air adequate to maintain combustion be regulated, but the stream of oil which drops on the pans or plates is under control of the workman operating the furnace. This method also permits of the smoke being taken away immediately from the flame, and thus prevents the black from being reburnt, which was one of the great disadvantages in the older process. It will be understood that the lampblack, to prevent loss of color, must be quickly removed from the flame.

The best grades of lampblack, generally speaking, are obtained in furnaces of moderate sizes so built that the black is practically calcined at the time it is deposited. It will then carry down little empyreumatic matter. The products of combustion are usually carried through a series of chambers in which there are baffles or partition walls. The gases carrying the lampblack are thus compelled to follow a tortuous path. The baffles cause the lampblack to be deposited out of the gas stream. Proper baffling may increase the percentage of decomposition of the raw material being burnt. Poorly designed baffles, or too great a number of baffles, may enforce gas velocities of such high rates so as to get the products of combustion through the system, that the gas stream may carry along the lampblack particles and not deposit them. Fig. 28 shows an arrangement of a lampblack plant.

It is very likely that future development of the lampblack industry will see the borrowing of ideas from other industries. We may see in the future the adaptation of the metallurgical bag house to a lampblack plant, or cyclone separators and tubular dust collectors or even a Cotrell elec-

trostatic precipitation unit at the end of a line of lampblack chambers. Certainly a modern lampblack plant, even advanced as it is in comparison to old methods, is still a very crude affair from a chemical engineering viewpoint.

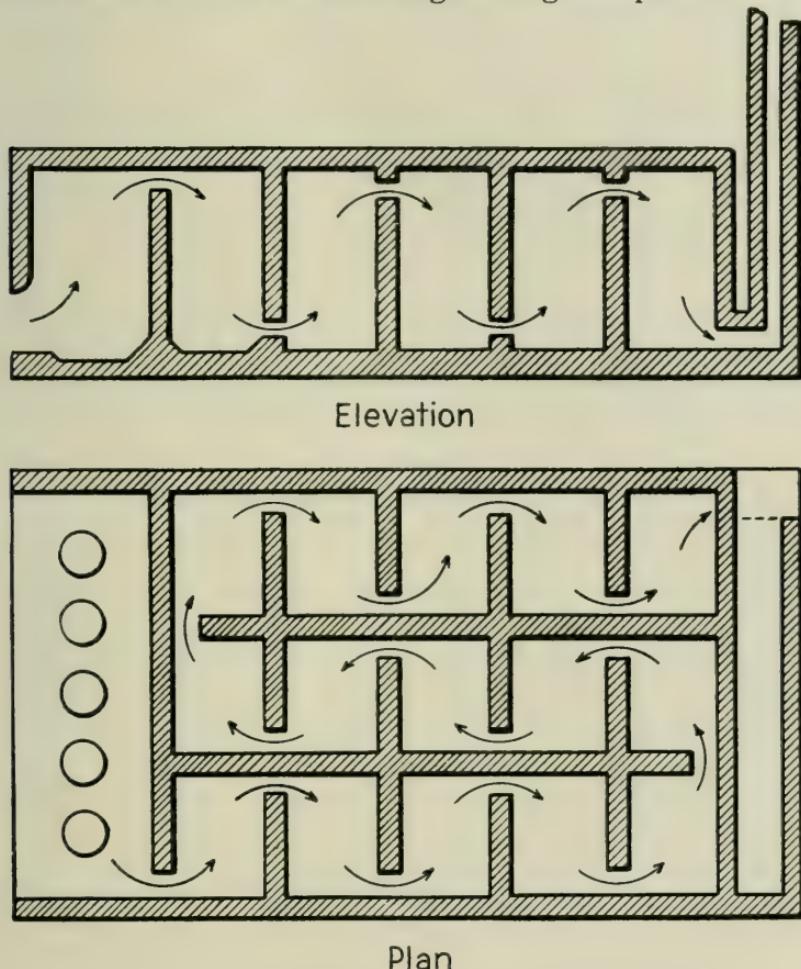


FIG. 28.—ARRANGEMENT OF A LAMPBLACK PLANT

In the pot type of lampblack works, the charging of the furnaces must be done quickly, to minimize the entry of large volumes of air. Excess air over that required for combustion may cause the formation of explosive mixtures with the

unconsumed combustible gases in the chambers. The furnaces are operated for the longest possible time consistent with economic collection of the lampblack. The chambers are then allowed to cool gradually. Small quantities of air are admitted at a slow rate to remove any combustible gases from the collecting chambers. The greatest care is necessary in cooling lampblack as it is very strongly pyrophoric. It is not removed from the chambers until thoroughly cool.

The future may see the development to a greater extent of continuously operated lampblack plants in which the product is removed from the furnace continuously and cooled more efficiently outside of the furnace.

There are very many grades of lampblack — more than of its sister black, carbon black. Some of it is shipped in sugar barrels packed full, containing only five pounds. The same barrel will hold 100 pounds of another grade. Chemi-

TABLE V
CHEMICAL ANALYSES OF LAMPBLACKS

Brand	Manufacturer	Method of Manufacture	Condition ¹	PROXIMATE				
				Moisture	Volatile Matter	Fixed Carbon		
Market 1	Patton Co.	Incomplete combustion of oil, probably "dead" oil.	1	0.39	2.26	97.35		
			2					
Market 2			1	3.12	17.38	79.44		
			2					
Germantown	Patton Co.	Incomplete combustion of oil, probably "dead" oil.	1	.39	2.26	97.35		
			2		2.27	97.73		
Lampblack 3	Binney & Smith Co.	"	1	3.12	17.38	79.44		
			2		17.94	82.00		
Lampblack 4	L. Martin Co.	"	1	2.47	14.66	82.87		
			2		15.03	84.87		

¹ Condition — 1. represents sample as received,

cally the two materials may be practically the same, but physically they are very different. The difference is due entirely to the amount of occluded gases and the particular shape of the particle. Lampblack particles are more like elongated tadpoles than anything else. They flock together not unlike floating cobwebs.

The gases so occluded are very interesting, containing various combinations of carbon, hydrogen, oxygen, nitrogen, and almost without exception, some sulphur. This sulphur originates in the coal; it persists in the processing of the coal to the tar; through the tar distillation to the heavy dead or creosote oil; and through combustion of the oil to the finished lampblack.

Lampblacks, being soots, contain exceedingly small amounts of ash, rarely running higher than a tenth of one per cent unless accidental dirt has been introduced. Table

TABLE V.—(Continued)
CHEMICAL ANALYSES OF LAMPBLACKS

Ash	ULTIMATE					CALORIFIC VALUE			Real Spec. Gr.
	Hydrogen	Carbon	Nitrogen	Oxygen	Sulphur	Calories	B.T.U.		
.00	.52	97.62	.11	1.18	.57
	.48	98.00	.11	.84	.57
.06	1.51	87.84	.00	9.95	.64
	1.20	90.67	.00	7.41	.66
.00	.52	97.62	.11	1.18	.57	7,986	14,375	1.70	
.00	.48	98.00	.11	.84	.57	8,017	14,431		
.06	1.51	87.84	.00	9.95	.64	7,386	13,295	...	
.06	1.20	90.67	.00	7.41	.66	7,624	13,723	...	
.10	1.76	88.94	.10	8.34	.76	7,484	13,471	...	
.10	1.53	91.19	.10	6.30	.78	7,673	13,811	1.72	

2. dried at temperature of 105° C.

V gives analyses of some commercial market blacks of the present day. The volatile matter of lampblack may vary over a relatively wide range, depending upon the methods of its manufacture. The uses of lampblack are discussed under paint pigments and ink pigments. Early in its history, lampblack was our most important printing ink pigment, but it has now been largely displaced in this particular field by carbon black (q.v.). In certain applications lampblack is considered superior to carbon black as a paint pigment in certain grey tints because of the bluish-grey tones of lampblack. Lampblack was formerly known under the name of gloss soot, light soot, flame soot and flame black.

CHAPTER XII

CARBONACEOUS INK PIGMENTS

CARBONACEOUS materials such as lampblack or related forms were used as the basis of the earliest known inks. All the ancient Egyptian inks were essentially carbonaceous in their composition. Almost all inks of the Sixteenth Century before Christ show, on examination, that they were of carbonaceous nature. Chinese or "India" ink, as it is now termed, was made as far back, according to oriental historians, as 2700 B.C. Vitruvius, a Roman engineer (30 B.C. to 14 A.D.), describes a decorative ink made from pitch pine soot. During the Middle Ages writing inks in Europe gradually changed from a carbon base to infusions of gall nuts and iron salts.

When Gutenberg invented the printing press and Caxton introduced it into England, lampblack came into universal use as a printing ink pigment. It was used to the exclusion of all other blacks until 1864 when carbon black became industrially important. In the early days of the industry great trouble was taken to purify the carbon black so as to allow the production of an extremely fine grained ink. With a lowered cost of carbon black after 1880 it was used to an ever widening extent, replacing lampblack. At the present time carbon black is the principal pigment for printing ink. Very little lampblack is used for that purpose and that only to impart certain qualities to an ink already containing carbon black as the principal base. Ink manufacturers and the printing trade have often stated that carbon black is absolutely essential to their industries.

Inks are made by mixing, grinding, and incorporating the pigments in boiled drying oils, such as linseed, perilla, tung,

and similar substances with driers and various other constituents such as varnishes, mineral oils, gums, fillers, petro-latum, etc., according to the specific qualities desired and the intended use for the ink.

Typographic printing, lithographic press work, depressed surface, plate or engraving impression are the three main classes of printing. Modern rotary presses require a rapidly drying ink, free flowing to permit high speed operation. At the same time the ink must have high hiding and covering power. It must make legible impressions instantaneously. Carbon black satisfies all these considerations. Nine pounds of ink containing one pound of carbon black and eight pounds of oil and other materials will print ninety copies of a three hundred page octavo book.

The modern newspaper is dependent in a physical sense upon three natural resources—our forests for its paper, our natural gas and oil for its ink. News inks are made by mixing carbon black and mineral oil in the approximate proportion of one pound of black to eight or nine pounds of oil. A single pound of carbon black thus mixed with oil will print twenty thousand pages of average newspaper size, or the equivalent of nearly an acre of surface. That is what is meant by "covering power."

The development of printing followed improvements in ink making. The desirable features of an ink are (1) suitable body, (2) proper cohesion or flow (long or short), (3) adhesion or tack. An ink varnish which drops away from a spatula with a long hairy drop is "long"; it is short when the drops come off sharply with a very small tail.

The black pigments which are with two exceptions (magnetic pigment and manganese black) carbon, are the most important ink pigments in wideness of use and quantity consumed. They are practically all good, different ones being adapted to different classes and processes of printing. One or two are valuable as additions to certain inks to improve their working qualities.

There are five classes of carbon ink pigments: (1) bone

black, (2) vine black, or vegetable black, (3) carbon black, (4) lampblack, (5) miscellaneous blacks.

Acid treated bone black has a deep black color due to its fineness. Its use as a toner for slightly off color or weak bone blacks and as a forcing black to bring up the color in certain classes of plate work makes it important. It is far superior to lamp or carbon black as a toner because of its lower oil absorption. The use of bone black, the most preferred form of which is drop black, is entirely restricted to plate printing inks. Bone black has a greenish black top hue and a brownish black under hue. It makes a somewhat short, fairly freely flowing ink. It is quite abrasive preventing the manufacture of smooth products. Its oil absorption is fairly low.

Vine blacks are termed "soft blacks" which describes their properties. They have a darker greenish black hue than bone black. Their fairly low oil absorption makes a somewhat long ink with moderate flow. They are quite abrasive and do not make up into smooth inks. The only field in which vine blacks find application is as toners for bone blacks in plate inks. Here they are of considerable value.

Carbon black has very great tinting powers and makes excellent typographical ink of fine working quality. The different brands and grades show a wide range of behavior in application. They vary from making short tacky inks to making some of great natural length and decided flow. Some carbon blacks, however, are worthless, not even being useful for making the cheapest news ink. Great differences will be found in the behavior of certain blacks toward driers. The reason for such extensive variation has not as yet been determined. By a proper combination of varnishes and grades of carbon black almost any desired effect in typographical printing ink can be secured.

Good grades of carbon black have a deep black top hue and a brownish black under hue. The material has a high oil absorption due to the exceeding fineness of the particles. It

ordinarily makes a short, poor flowing ink which is remarkably fast to light and resistant to atmospheric influences. Good grades of carbon black exert no drying action. They are not abrasive and work up to a very smooth ink. Carbon black is the most important typographic black, being the basis of practically all black typographic inks to-day.

Lampblack has a deep black top hue and a brownish black under hue. Like carbon black, it has a high oil absorption but makes short ink with poor flow. Many of its properties are similar to the cheaper carbon blacks which have displaced it, but it does not give inks of the best consistency and it is too gray in color.

Miscellaneous carbonaceous blacks used in printing are mineral black and the mixed blacks. Mineral black is a 30% carbon shale, washed and ground to a fine soft powder. It is sometimes used in making very cheap blacks for plate printing inks. Mixed blacks are made up from bone blacks, vine blacks and various carbonaceous materials with a view of overcoming the defects of straight mixtures of bone and vine blacks. They contain 30% to 50% ash (of which 5% is insoluble in hydrochloric acid), the rest being carbon. They are used only for plate printing. The mineral blacks are brownish black in color with a decided brown under hue. They make long inks which are not smooth. The material is quite abrasive. The oil absorption of both the mixed and mineral blacks is low. Mixed blacks have properties which are dependent upon the properties of their constituents. In many respects they are analogous to lampblack.

Plate inks made from carbon black or lampblack will not work satisfactorily as they lack grain and body and have too high an oil absorption. The highest grade of plate ink is made from pure acid-washed bone black, finely ground and brought to the proper color by the addition of high grade vine black and enough Prussian blue to develop the black fully but not enough to blue the under hue.

The properties of the various important carbonaceous ink pigments are summarized in the following tables.

TABLE VI
PROPERTIES OF BLACKS
(from Underwood and Sullivan)

<i>Name</i>	<i>Top Hue</i>	<i>Under Hue</i>	<i>Oil Absorp-tion</i>	<i>Fineness</i>
Bone black	Greenish black	Brownish black	Fairly low	Should be fairly fine, that is, they should still have some grain
Vine black	Greenish black darker than bone black	Brownish black	Fairly low	
Carbon black	Deep black	Brownish black	High	
Lampblack	Deep black	Brownish black	High	
Mineral black	Brownish black	Decided brown	Fairly low	Should be impalpable powders

TABLE VII
PROPERTIES OF BLACKS
(from Underwood and Sullivan)

<i>Name</i>	<i>Flow</i>	<i>Shortness</i>	<i>Fastness to Light</i>	<i>Atmospheric Influences</i>
Bone black	Flows fairly well	Fairly short		
Vine black	Flows fairly well	Fairly long		
Carbon black	Poor	Short		
Lampblack	Poor	Short	No effect	No effect
Mineral black	Good	Fairly long		

TABLE VIII
PROPERTIES OF BLACKS
(from Underwood and Sullivan)

Name	Drying	Smoothness	Abrasive Qualities	Incompatibility
Bone black		Does not make a smooth ink	Quite abrasive	
Vine black		Does not make a smooth ink	Quite abrasive	
Carbon black		Works up very smooth	Not abrasive	
Lampblack	Exert no drying action	Works up smooth	Not abrasive	Mixes with everything
Mineral black		Does not make a smooth ink	Quite abrasive	

TABLE IX
PROPERTIES OF BLACKS
(from Underwood and Sullivan)

Name	Value as an Ink-making Pigment
Bone black	Of great value as a plate printing ink material although it must be mixed with vine black for color and to give the proper working qualities.
Vine black	Of great value as a toner to mix with bone black to give color and working qualities to black plate printing inks.
Carbon black	The most important typographical black, in fact it is the base of all black typographical inks at the present day.
Lampblack	Not much used at present as its place has been taken by the cheaper but similar carbon black.
Mineral black	Used principally to mix with other blacks.

According to ink manufacturers, various grades of carbon black show very different properties when made into ink. Underwood¹ says: "There is a wide range in the behavior of different carbon blacks, a wider range than there is any apparent cause for."

The terms "length" and "shortness" are explained by Underwood as follows:

"If a pigment when mixed with a large quantity of oil still remains stiff or can not be drawn out into a string between the fingers but breaks, it is said to be short. While there are some classes of work that require ink of a certain degree of shortness, as a general rule pigments that show this quality are not suited for making inks.

"An ink that flows well must also have the property of being drawn out into a string between the fingers, and this is called length. Thus each of these terms suggests or includes the other; they are both sometimes spoken of under the name of viscosity."

Apparently a pigment that gives a long ink is one that affects the original properties of the vehicle to a less extent than does an equal weight of a short pigment. To a large extent this question is probably one of fineness of subdivision, although the tendency of the particles of the pigment to form agglomerates may also affect it.

In general, the higher the percentage of carbon in the black, the blacker it looks under the microscope. The particles are extremely small, indications being that their average size is about 100 millimicrons. Particles of long blacks are slightly larger than those of short blacks. Under the microscope freshly prepared mixtures of thin lithographic varnish with short and long carbon black at first appear precisely similar. They seem to consist of agglomerates of two or three or more particles. The short black after a few minutes agglomerates into groups of 20 or 30 particles, and

¹ Norman Underwood & T. V. Sullivan: The Chemistry & Technology of Printing Inks (1915) p. 67.

in an hour larger aggregates form. Long blacks remain completely dispersed after several hours. Fig. 29 shows a short black two hours after preparation on the slide. Fig. 30 shows a long black after several hours at 500 magnifications. These microphotographs are taken from Bulletin No. 192 of the Bureau of Mines. The concentration of



FIG. 29.—SHORT BLACK TWO HOURS AFTER PREPARATION

ON SLIDE. MAGNIFIED 500 DIAMETERS

(Courtesy Bureau of Mines)

blacks in oil on the slides is about one part in one million parts of oil.

Cool flames and cylindrical burners, which are methods having a tendency to produce blacks high in volatile matter, give long blacks. It is assumed that the adsorbed impurities prevent agglomeration of the carbon particles. If a long black be treated with steam at 500° C. so that the occluded matter is burned off, the black is seen to be agglomerated

under the microscope. If short black be treated with a dilute alcoholic tannin solution dried and mixed with oil, it makes a much more fluid mixture than an equal amount of untreated black. Agglomeration tendencies are materially modified by the vehicles used in ink making. In thick viscous varnishes no agglomeration is noticeable after several hours.

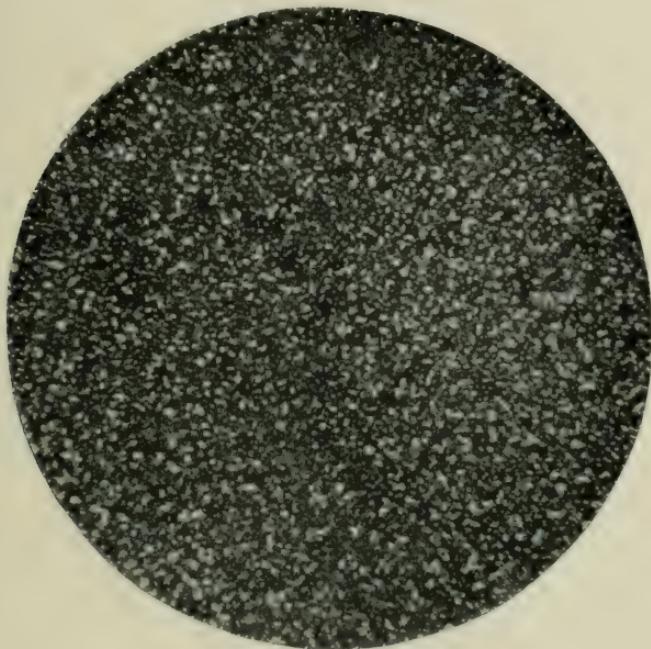


FIG. 30.—LONG BLACK TWO HOURS AFTER PREPARATION
ON SLIDE. MAGNIFIED 500 DIAMETERS
(Courtesy Bureau of Mines)

Metallic soaps in small amounts tend to cause particle gathering even when long blacks are used. The tendency for particles to group themselves together does not entirely explain the difference in the behavior of different blacks. It is very probable that surface forces between the vehicle and the particles of black, as well as the size of the particles, are of considerable importance.

Lampblack and the different grades of carbon black look

very much alike under the microscope. Lampblack is sometimes a little blacker and more opaque. Some commercial products have a larger percentage of coarse material, but the divergence in properties is possibly due to differences in composition of the exceedingly minute particles, possibly differences in size or constitution, the attraction between the particles, and surface energy reactions at the oil-lampblack

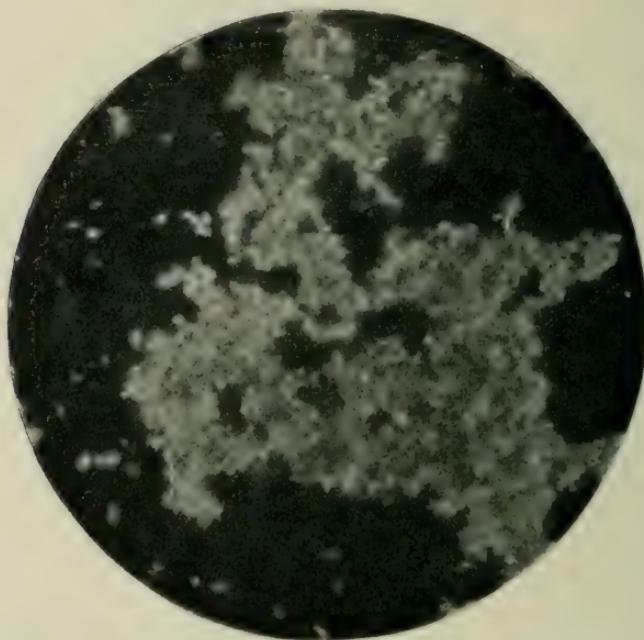


FIG. 31.—LAMPBLACK, MAGNIFIED 2,000 DIAMETERS
(Courtesy Bureau of Mines)

interface. Differences in surface conditions apparently due to the presence of adsorbed gases and combined oxygen, may account for differences in lampblacks and carbon blacks. A lampblack which is calcined at too high a temperature contains too little empyreumatic matter and adsorbed gases, and produces a short ink. Fig. 31 shows a micro-photograph of commercial lampblack at 2,000 diameters.

Long inks probably contain blacks consisting of slightly

larger particles than those used in short inks. Less surface per unit weight is exposed in the long ink and less oil is required to make a mixture of a given consistency. Differences in surface conditions, due to the fact that long blacks contain a high percentage of adsorbed gases, affect the properties of the mixture of the black with oil. Under the microscope it is seen that blacks containing large amounts of volatile matter remain dispersed while those containing small amounts of adsorbed impurities agglomerate.

CHAPTER XIII

BLACK PAINT PIGMENTS

BLACK pigments find extensive use in various branches of the paint industry. The most important black paint pigments, given in the order of volume used, are carbon black, lampblack and graphite. Other blacks such as the Frankfort blacks, bone black, ivory black and mineral black are used but to a much smaller extent. In the order of their importance, the chief physical properties to be looked for are as follows:

1. Color.
2. Tinting strength.
3. Fineness.
4. Oil absorption.
5. Specific gravity.

The term color refers to the relative blackness of a material when mixed with oil. Usually this is only comparative.

The tinting strength of a pigment is its most important property in the eye of the paint manufacturer. The tinting strength as applied to blacks is a measure of their ability to impart a gray hue to a definite weight of a standard white pigment. Both lampblack and carbon black are simply extremely fine shades of some color, there being no absolutely perfect black, as each of them shows faint traces of the three primary colors: red, yellow and blue, in their various combinations, carbon black having apparently more red and yellow combined than blue, whereas lampblack has more blue and yellow than red.

This may be noted by rubbing one part of each pigment in a hundred parts of zinc white made into a paste with sufficient clear colorless oil. The result will be two slaty gray shades, one with a decided reddish brown or bronze appear-

ance, and the other, more of a soft blue-gray dove tone. The smokes from the factories have this same characteristic difference, one being of a brownish color and the other of a light blue-gray.

The hiding power of a pigment is inversely proportional to the diameter of the particles. The finer the particles of a given pigment are when they are mixed to form a paint, the greater is its covering power.

The amount of oil or other medium required to convert a pigment into a paste ready for application in painting is termed its oil absorption. This varies with the air voids in the material, the wetting power of the oil, the nature of the surface of the solid particles, the fineness of the pigment and the geometrical arrangement of the solid particles in the paste or paint. The bulking value and oil absorption of some carbon pigments are given below:

Pigment	Bulking value lbs./c. ft.		Air voids % for packed condition.	Oil absorption in gms. of oil per 100 gms. of pigment.
	Loose	Packed		
White lead A	44	125	71	12
Barytes	49	140	49	13
Carbon black	13	23	80	150
Ivory black	19	53	58	46

Gardner¹ has given some figures showing the percentage of oil required for grinding pigments into average paste form, viz.: carbon black, 82%, lampblack, 72%, drop (bone) black, 60%, bone black, 40%, graphite (pure), 40%, and for contrast one may cite white lead (sublimed), 10%, blanc fixé, 30%, barytes (natural), 9%, terra alba (gypsum), 22%.

The specific gravity is important as it affects to a considerable extent the volume of the finely mixed paint as well as the behavior of pigments when suspended in liquid media. The effect of fineness is seen in the amount of oil required to grind the pigment into a uniform stiff paste. The table gives average specific gravities for some of the black pigments as compared with others:

¹ "Paint Technology and Tests," 1911.

Average Specific Gravity of Black Pigments with Others for Comparison

Graphite	2.46	Red lead	8.80
Drop black	2.46	Zinc oxide	5.60
Bone black	2.35	White lead	6.60
Lampblack	1.78	Barytes	4.45
Carbon black	1.80	Ultramarine blue	2.50

Bone black is sometimes used for decorative work in preference to other forms of black. Carbon black, however, may be added to deepen the tone. Such pigments are commonly cheapened by mixing with barytes and whiting.

For tinting and staining purposes, either lampblack or carbon black is generally used. All blacks do not possess the same strength of color or tinting power. Carbon black has a much greater tinting strength than lampblack. Although the tinting strengths of various commercial grades of carbon black and lampblack show great variations, approximately five times as much lampblack is ordinarily needed to do the same tinting work that one part of carbon black does. Carbon black, in certain of the best grades, may have as high as ten times the tinting strength of mineral blacks.

Carbon black is acknowledged superior for varnishes and enamels. It is much used in making black and gray paints for general purposes. Its use is required in enamels in various black and gray paints to be supplied to the United States War Department. According to Toch,² lampblack is a superior pigment to carbon black, and it is probably true that in certain gray tints lampblack is superior on account of its bluish-gray tones. Lampblack is specified in paints for the United States Navy.

Because of their fine state of subdivision, carbon black and lampblack absorb a larger quantity of oil in grinding than do the mineral or the bone blacks. Various miscellaneous blacks are sometimes used as toners in black paints,

² M. Toch, Chemistry and Technology of Paints.

and mineral black may be added to cheapen a paint and act as an inert.

The use of graphite in paint is in a class by itself, for its action is not ordinarily that of a pigment but of a protecting medium. It is used extensively as the pigment in paints that are called upon to withstand the corroding action of sulphurous gases, acids, alkalies and the like. It is especially valuable for covering metal surfaces and roofs in a smoke laden atmosphere as well as structural steel work in all its various forms.

There is considerable diversity of opinion as to the most suitable kind of graphite for graphite paints. The natural amorphous, the natural flake, and artificial varieties are all employed. The most successful paints, however, are those made with lower grades of natural flake graphite.

The purer a carbonaceous paint pigment is, the poorer is the paint produced. If an 80 to 90% carbon graphite be mixed with linseed oil, it forms a porous, fluffy film. Coagulation of the graphite particles occurs and a very unsatisfactory covering is produced. If the graphite is mixed or diluted with a heavier inert material, its weakness becomes its strength and a very good paint is formed. Many of the chemical and physical defects of red lead are largely reduced when it is mixed in proportion with graphite. A high grade of graphite used in this way, finely ground in linseed oil, acts as a lubricant and slides under the brush. The covering power of pure graphite paint is from 1,000 to 1,600 sq. ft. to the gallon. The paint film is so exceedingly thin that in a short period decomposition readily takes place. This decomposition is often much more rapid than the rate of very poor paints. It is essential to incorporate with the graphite a heavier base. A silica and graphite mixture produces very good results with the objection, however, that the product has too great a spreading power. Many of the natural graphite paints perform in an exceedingly satisfactory manner. They are natural mixtures of graphite, silica, and other mineral constituents closely bound together and in a

flake form. In the paint film, these flakes tend to assume positions parallel to the painted surface, the flakes overlapping each other. Such a paint has a "tooth" as compared to one made of a pure graphite with mixtures of silica. The latter has the defect that when a large amount of graphite is incorporated in the paint, a smooth and satin-like film results. This is poorly adapted to repainting or second coating. It has often been noted that a good slow-drying linseed oil paint will curl up when applied over certain graphite paints because it does not adhere to the graphite film. On the other hand, if particular forms of calcium carbonate, silica or ferric oxide are added to graphite, a surface is presented which has a tooth to which succeeding films adhere very well.

Artificial graphite is commended by Toch as a paint material on account of its uniformity and fineness of grain. It should not be used alone, however, as a pigment, for as such it possesses the physical defect of lightness. When a considerable quantity, say up to 40 to 50%, of inerts or of lead and zinc pigments is added, a very satisfactory paint is made.

Tests extending over several years, of linseed oil paints made with ferric oxide containing in its composition 75% ferric oxide and 20% silica mixed with 85% graphitic carbon graphite, have proved this material to be as good a paint as can be desired for ordinary purposes. It is strongly resistant to the chemical action of corroding gases and fumes. The oil vehicle, however, is its weakest part.

A number of misnomers have crept into the paint trade in regard to graphite paints, such as green graphite, red graphite, aluminum graphite, brown graphite being used. In reality, of course, such graphites do not exist. These paints contain enough graphite to make them protectors against corrosion, and their coloring is due to the additional pigments added giving the desired effects. Red graphite paint, consisting of mixtures of graphite, red lead, silica, and various other pigments and inerts, is extensively used on bridge structures and structural steel frame works.

CHAPTER XIV

MISCELLANEOUS BLACKS

THE various carbons, or rather the materials of carbonaceous nature which are known to the trade as carbons, such as gas retort coke, oil retort coke, graphite, carbon black, wood pulp black, willow charcoal, Frankfort and vine blacks, bone black, ivory black, sugar house black, and blacks made from refuse materials such as various organic scrap products, do not all possess the same flocculent characteristics, strength of color, chemical composition or physical structure. Each black has its own specific uses and as a rule can not be substituted for another black. To apply the usual tests to determine which black to use is often difficult because of the modification in properties when a black is combined with other substances.

Gas retort and oil retort coke are discussed specifically under raw materials for electrode manufacture. Graphite, carbon black, lampblack and bone black are each discussed separately.

There is a characteristic difference between the smoke of a burning product, and the charcoal or coke of the same product. All carbonaceous materials give up their volatile matter when burnt with an insufficient supply of air in a closed retort. The residue after distillation is charcoal or coke. Commonly we talk of the charcoal of wood, bone, leather, rice hulls and similar materials. We speak of the coke of coal and of petroleum oil. When wood or bone is distilled, the charcoal may be properly described as the skeleton of the material from which the volatile constituents have been driven off, with or without decomposition. The charcoal is in fact the skeleton, for it retains the framework, the grain

and structure from the wood or bone from which it is derived. Microscopically it is easily possible to determine the structural differences between charcoals from different woods, for all the charcoals have different characteristics. For example, that of the willow is the softest of charcoals, while that made from the oak is hard and harsh. Charcoals of wood, bone, ivory, etc., are all black when destructively distilled, but all of them retain the grain and structure of wood, bone and ivory in just the same manner as the coke of coal is the skeleton of the coal.

Benzol black is a soft non-granular black made from benzol in a manner similar to carbon black made from natural gas. It remains in suspension longer than carbon black in oil and varnish. It is however regarded as a poor drier.

Drop black is a pigment made from bone black which no longer has sufficient color removal properties to justify its further use by the sugar manufacturer. The "spent" bone char is thoroughly washed and ground in burr stone mills to reduce the spongy carbonaceous matter to a fine silky powder. The old custom was to sell this black in lumps made by dropping the black paste, as it came from the grinding mill, in little heaps on boards for drying. The following out of this prescribed ritual and the production of the black in peculiarly shaped pieces, was a criterion of purity. To some extent even today this procedure has to be adopted to satisfy those users who are unconvinced of the purity of finely ground bone black sold in the form of a powder.

Present day drop black is made by calcining sheep bones, grinding them in various ways to an impalpable powder. While still in a paste form, the material is cast into small cone shaped drops. The name "drop black" as used by the trade also applies to finely powdered bone black. It contains 10 to 20% carbon and 80 to 90% calcium phosphate. It is used as a pigment to a small extent for various types of inks, sometimes in paints and miscellaneous uses.

Ivory black or "extract of ivory black" was formerly made from charred ivory chips which have been digested in

hydrochloric acid to dissolve out their calcium phosphate content. It possesses intensely black staining power. It is colloidal in nature. The present day ivory blacks are forms of bone black made by the dry distillation of the best quality of bones obtainable after steaming, rendering, and defatting. It is more intense in color than the average quality of bone black. Because of its cost, it is used only for ready prepared colors as a "toner" and in high grade enamels.

Mineral black is a black pigment made by finely grinding a clay shale or slates containing about 30% carbon. When properly prepared by washing and grinding, it forms a fine soft powder. It is sometimes used for making mixed blacks for plate printing inks and as a cheap paint filler and pigment.

The shales from which mineral black is made are widely distributed. Some occur in an especially pure state in Spain, less so in Switzerland, the Tyrol and Italy. These are generally blue black to brownish black in tint. Large deposits suitable for making mineral black exist in the United States and Canada. Some of these are deposits of disseminated graphite in decomposed rocks.

Certain mineral blacks are produced by carbonizing waste coal dust and Scotch bog material in retorts and grinding the result to a fine powder.

Mineral black has only a low tinting power, though it finds use as an inert pigment in compounded paints. It has a flocculent appearance. The particles show a strong tendency to mass.

Mixed blacks are made from bone blacks of various kinds, vine blacks and different miscellaneous combinations with a view to adding certain qualities or overcoming certain defects.

Special blacks are made for various purposes, particularly for adding to other materials, from coke, lignite and certain by-products. One of these is blood black, made by charring blood. It is very soft and has strong adsorbing power for alkaloids and coloring matters. Another is leather black,

made from waste and scrap leather. The ash, carbon content and properties vary with the raw material.

Swedish black is a pigment which is in effect a modified lampblack. It is made from the bark of the silver birch tree. The material is packed into retorts and carbonized. The result is a mixture of charcoal and lampblack. It finds miscellaneous applications as a pigment.

Vine black refers to those pigments produced by the dry distillation and carbonization of willow wood, wine yeast, grape husks, grapevine twigs, spent tan bark, shells, fruit pits, sawdust or in fact any material of vegetable origin.

The blacks produced from grapevine twigs, grape husks, and wine yeast are the best of this class. The name "vine black" refers to the fact that formerly only these materials were used to produce it. The name Frankfort black was also used. At the present time, however, this name has been extended to take in every variety of black of vegetable origin. They are also termed vegetable blacks.

TABLE X
ANALYSES OF MISCELLANEOUS BLACKS

Brand	Manufacturer	Condition ¹	PROXIMATE			
			Moisture	Volatile Matter	Fixed Carbon	Ash
Bone black	Binney & Smith	1	3.88	10.92	2.68	82.52
		2		11.36	2.79	85.85
		3		80.28	19.72	
Vine black	Binney & Smith	1	9.58	29.54	40.50	20.38
		2		32.67	44.79	22.54
		3		42.18	57.82	
Willow charcoal	Binney & Smith	1	3.24	14.66	80.23	1.87
		2		15.15	82.92	1.93
		3		15.45	84.55	
Wood-pulp black	Binney & Smith	1	6.42	9.78	78.84	4.96
		2		10.45	84.25	5.30
		3		11.04	88.96	

¹ 1 denotes sample as received; 2, dried at a temperature of 105° C.; 3, moisture

These vegetable blacks, when properly made, are of a deep black color and show great strength. They analyze about 75% carbon and 25% ash. The ash consists of silica, calcium carbonate, sulphate and phosphate and a small amount of potassium carbonate.

The vegetable blacks in the order of their quality, are graded as follows:

1. True vine black, that is, the product made from wine yeast or grape fruit twigs.
2. Blacks from grape husks.
3. Blacks from willow charcoal, specifically termed willow black.
4. Blacks from spent tan bark.
5. Blacks from fruit pits.

The quality differences are due entirely to the differing physical properties exhibited by the products from different sources. These are differences in density, grain, and state of division and physical characteristics such as hardness or

TABLE X—(Continued)
ANALYSES OF MISCELLANEOUS BLACKS

ULTIMATE					Calories	B.T.U.	Real Specific Gravity
Hydrogen	Carbon	Nitrogen	Oxygen	Sulphur			
0.88	8.64	1.06	6.84	0.06	668	1,202
.47	8.99	1.10	3.53	.06	695	1,251
3.32	63.53	7.77	24.96	.42	4,912	8,842
2.44	51.65	.80	24.41	.32	4,079	7,342
1.53	57.12	.88	17.58	.35	4,511	8,120	2.02
1.98	73.74	1.14	22.69	.45	5,824	10,483
2.74	85.04	.16	10.11	.08	7,514	13,525
2.46	87.89	.17	7.47	.08	7,766	13,979
2.51	89.62	.17	7.62	.08	7,919	14,254
1.60	83.20	.17	9.59	.48	6,973	12,551
.95	88.91	.18	4.15	.51	7,451	13,412
1.00	93.89	.19	4.38	.54	7,868	14,162

and ash free.

softness. Many of the characteristics are functions of the manner of carbonization and after treatment.

Many Frankfort and vine blacks made in the United States today are mostly made from wood pulp black, a material obtained as a by-product of paper manufacture. These blacks are similar to those originally made in Germany.

The vine and vegetable blacks are made by carbonization in a suitable retort, of which there are many different forms, with or without the recovery of by-products. After the material is burned, it is washed with water to remove the soluble salts. The finest grades are acid washed in addition. The vine blacks are used in the plate printing trade, where they are called soft blacks. Their principal use is to give a certain grain and to give increased color. Essentially all the vegetable blacks are charcoals.

Chemical analyses of some of the blacks are given in Table X.

CHAPTER XV

CHARCOAL AS FUEL

IN this chapter we will confine our efforts to the discussion of charcoal as a fuel, its manufacture, and its industrial applications. Activated carbons and manufactured charcoals, such as those used in deodorizing, decolorizing and metal removal from solution, are discussed in detail under their respective headings.

Charcoal is the more or less impure form of carbon obtained from the various vegetable and animal matters by their ignition out of contact with air. Wood charcoal is a hard, brittle black substance which retains the form and external structure of the wood from which it is made. It rings when struck and has a conchoidal fracture. It is infusible, is not dissolved by water or acids, and at ordinary temperatures is a poor electrical and thermal conductor. Charcoal varies much in degree of compactness, boxwood giving a very hard, and willow a very soft, variety. Its true specific gravity when made at low temperatures is of the order of 1.5, or if made at a high temperature, of 2.0. Its apparent density will vary from as low as 0.2 to as high as 0.5. The higher the temperature at which it has been made, the higher will be its ignition point.

All the parts of trees and shrubs which in industry and everyday life are described as "wood," may serve as the raw material for charcoal manufacture. Wood in this sense covers the main mass of the trunk, the branches, and the roots.

The particular class of material of most importance to the charcoal maker is so-called fuel wood or fire wood, obtained in the forests as the residue after the timber pit wood

and pulp wood for paper making have been selected from the felled trees. This comprises split billets, rounded billets, brushwood, and stumps. In recent years another class of material consisting of various forms of scrap wood, obtained as a result of mechanical treatment of timber in saw-mills, has been successfully used for carbonization. Waste wood, — slabs, laths, resulting from sawing, — is now used for carbonization. Formerly, sawdust was fed under boilers and was not successfully carbonized; at the present moment, however, charcoal briquettes are manufactured in large tonnages as a result of the carbonization of sawdust. In many countries, particularly those in which the oil seed industries are large, fruit stones, palm nut shells, coffee husks and especially olive stones in Spain and Italy, are used for carbonizing and charcoal manufacture. The usual case, however, employs only forest or saw mill waste.

The woods are classified as hard or soft, according to the compactness of their cellular tissue, their specific gravity, and their resistance to mechanical treatment as expressed in their tensile and compressive strength. The charcoal yields from the various woods will vary with the properties of the woods. The trees may be roughly subdivided into the broad-leaved containing a predominating amount of extractive matter, and the coniferous which yield large quantities of ethereal oils and resins. A wood classification is given below:

Very hard — hawthorn

Hard — maple, hornbeam, wild cherry

Moderately hard — oak, plum, robinia, elm

Rather hard — beech, walnut, pear, apple, sweet chestnut

Soft — spruce, silver fir, Scotch pine, larch, alder, birch, ash, horse chestnut

Very soft — lime, poplar, willow

The broad-leaved woods produce a larger yield of acetic acid and methyl alcohol when subjected to destructive distillation; the coniferous a higher yield of tar; the charcoal is

approximately the same for all the woods. The rate of carbonization will decidedly affect the quantity of charcoal produced. A tabulation is given below of various woods showing the yields of charcoal when subjected to slow carbonization and to rapid carbonization:

	Slow Carb.	Rapid Carb.
Hornbeam, trunkwood	25.37	20.47
Alder, small trunkwood	26.5	22.53
Adler, sound peeled trunkwood	31.56	21.11
Birch, sound trunkwood	29.24	21.46
Mt. ash, sound trunkwood	27.84	20.20
Beech, sound trunkwood	26.69	21.90
Beech, sound branchwood	26.19	21.30
Aspen, sound trunkwood	25.47	21.33
Beech, blighted branchwood	23.23	20.98
Oak, sound trunkwood	34.68	27.73
Larch, sound trunkwood	26.74	24.06
Spruce, sound branchwood	25.55	23.35
Spruce, bark	30.24	31.59

When charcoal only is desired, the simplest and crudest form of distillation is the common charcoal pit, shown in Fig. 32. In China practically all charcoal is prepared in this manner, preferably in a clayey soil. In some parts of

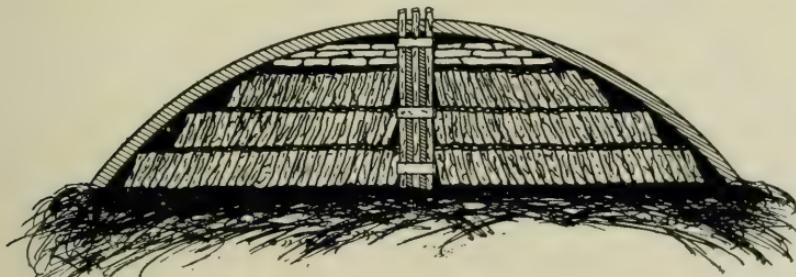


FIG. 32.—CHARCOAL PIT

Sweden it is made from rectangular piles of wood, the process being regulated by the careful admission of air through holes in the covering of the wood. In most countries where

wood is abundant, charcoal burning is carried on by firing conical piles of billets of wood from twelve to fifteen feet in height and ten to fifty feet in diameter. Wood is felled in winter and must be ordinarily dry. The pile is built up with the bark outermost, the largest billets being placed in the center of the pile. Over the whole is laid a covering of turf or clay or of charcoal dust and soil. The combustion of wood is conducted from above downwards, and from the exterior toward the center, so that the charcoal in a half burned heap forms an inverted cone. At the sides of the heap are holes for the admission of air, the number and size of which are determined by the experience and judgment of the charcoal maker. In this form of distillation, part of the wood is carbonized by the heat formed by the combustion of another part. Water vapor is driven off first and the oxygen of the air absorbed in the wood is consumed. As carbonization proceeds, the pile "sweats," that is, the covering becomes moist with condensed water. The openings around the base of the pile are then covered and a series of holes made about half way from the top of the heap. As the smoke ceases to issue from these, they are closed and other openings made in various parts of the heap formed as required. The charring is finished when the gases issuing become light blue in color. The tarry products resulting collect toward the close of the operation in the crude gutters at the base of the pile. When carbonization has been judged to be complete, the earth, clay or turf covering the pile is removed in small sections at a time and the charcoal quenched either with cold sand or water. The charcoal heaps built up and operated in the manner described are called "meilers."

The charcoal meilers, with their slow rate of oxidation and long interval between initial and final temperatures, produce yields of charcoal which, in spite of admission of air and most primitive methods of operation, are equal to those obtained from the more scientifically built retorts or kilns.

In a charcoal kiln the wood is stacked either on end or

lying down. The kiln itself consists of a brick chamber either beehive in shape or rectangular. As in the meiler, a passageway is left to the middle of the pile so that a fire can quickly reach the center. The most modern kilns are of brick with door openings in the top and bottom for charging the wood and discharging the charcoal. Stacks to induce draft with flue connections to the kiln are the usual method of construction. Some plants employ forced draft fans which allows them to have a charcoal manufacturing cycle of approximately 11 days as compared to 21 to 24 days without forced draft. As with the pit, the presence of the light blue vapors issuing from the stack denotes the fact that most of the volatile matter of the wood has been driven off. The kiln is then closed up tightly with lime and allowed to cool.

It will be noted that in both the meiler and the kiln method of carbonization, all the by-products in the form of condensable vapors are lost. To save the volatile matter coming from the wood, various retorts have been devised. These differ quite markedly in construction according to locality, the kind of wood distilled, and the engineering opinions of the designers. The simplest form of retort consists of a totally closed vessel with suitable openings, surrounded by or mounted in a furnace to which heat can be supplied by any of our known means. Some kind of receiver is needed in which the condensed products may be collected. Where there is acid the retorts are made of iron, the connecting pipes and condensing tubes of copper and the receiving tanks of wood with or without copper linings.

The retorts used are of two distinct types, vertical and horizontal. The horizontal type is subdivided into those of rectangular shape and those of cylindrical shape. The vertical type is subdivided into the fixed retort, the movable retort, and the fixed retort with removable cage.

The present day retort construction calls for the use of $\frac{1}{2}$ " boiler plate. Cast iron and clay were formerly used as materials of construction, but their use has diminished due

to the low mechanical strength of these materials and their disadvantage of cracking when heated too rapidly.

Of the horizontal retorts, the ovens as shown in Fig. 33 are the most numerous. They are rectangular in shape, slightly arched on the top and flat on the bottom. Exits for

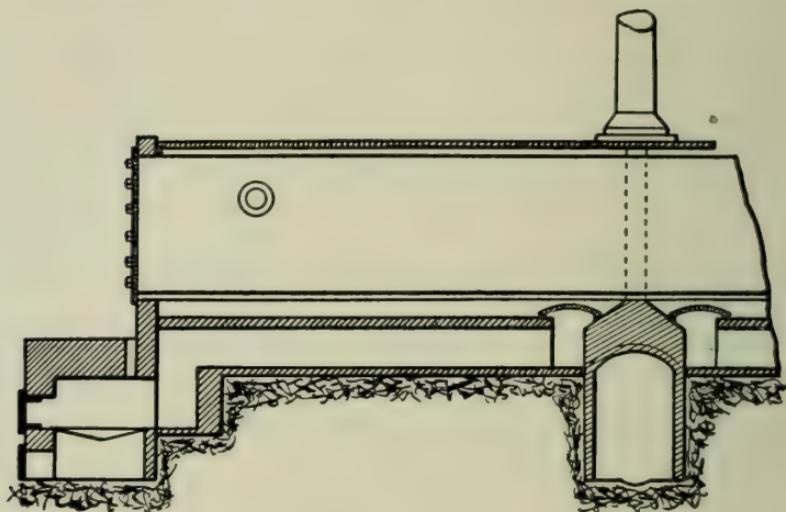


FIG. 33.—STEEL OVEN, HORIZONTAL TYPE

the vapors are provided either at the sides or at the back. The wood is loaded on steel cars holding about two cords each and rolled into the retort. The ovens are about six feet wide and seven feet high and of various lengths to hold differing numbers of cars of wood. One or two coolers are used with each of these ovens. The coolers are of similar construction to the ovens but of lighter material. After carbonization, the trucks are pushed from the retort into the cooler, where they may reach room temperature without oxidation.

Some of the cylindrical retorts, as shown in Fig. 34, are made about 9 ft. long by 50" or so in diameter. Their capacity is about a cord of wood. They are charged and emptied manually. An iron box mounted on wheels is used

to hold the charcoal and when it is full it is covered with a sheet iron cover. The cover is luted with sand or clay.

No particular type of vertical retort seems to be preferred. They are usually cylindrical with capacities of $\frac{1}{2}$ to 7 cords. The fixed retorts remain in the brickwork, and are connected to the vapor pipe of the condenser by one or two pipes, preferably one at the top and one at the bottom. The movable retorts are so arranged that they can be pulled out of the furnace when carbonization is finished and allowed to cool unopened. A modification of the movable retort consists of a removable cage fitting inside of the chamber. Only the cage is removed, and as it does not have to stand the

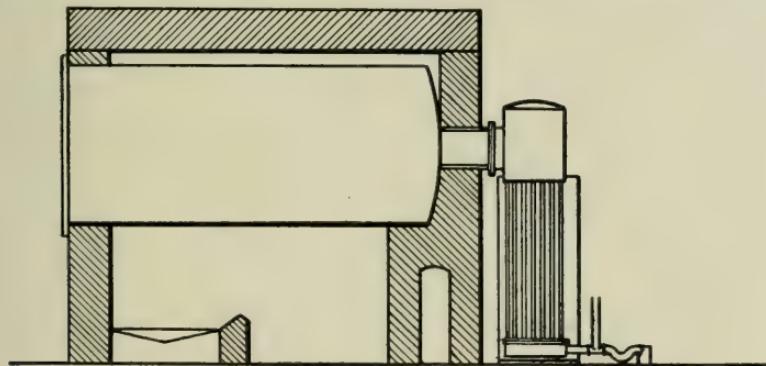


FIG. 34.—CYLINDRICAL RETORT AND CONDENSER

direct heat of the fire, it may be made of lighter material than the retort itself.

Inasmuch as we are interested here only in charcoal production, the reader is referred to other works for information and data on other products of destructive distillation, such as acetic acid and methyl alcohol.

The retort in its various forms is the most efficient piece of apparatus for wood carbonization. Practically all the by-products are saved. No air, or only a regulated amount, is admitted, but on the other hand distillation is carried out more rapidly and the initial temperature is higher. Ordinarily, the charcoal yield is no greater than that produced in meilers, but on the other hand, it must be noted that the

weight of charcoal produced in pits is considerably enlarged owing to water quenching. This explains why the yields are apparently equal to those from the retorts.

Charcoal from slow carbonization is richer in carbon. Although the carbon content is regulated by the temperature at which carbonization is completed, it also depends on whether the charcoal cools in the carbonizing apparatus itself or elsewhere. The absorption of hydrocarbons effects an increase of about 6% in the carbon content. The greater the distillation rate, the higher the initial temperature, the shorter the time between initial and final temperature, the lower is the yield of charcoal.

Below are given some tables showing the charcoal yields from meilers and those of cooled char from retorts.

TABLE XI

	Char		Acetate of Lime 80 %		100 % Crude Naphtha		Tar		Pine Oil	
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
European beech . .	33	28	10.5	8	2.5	1.7	6	5		
American maple . .	35		8		2		7			
Pine — very rich in resin — Georgia	33	28	2.5	2.3	.42	.28	20		8	
European silver fir	36	33	3.6	3.0	.8	.6	12		5	.4
Sawdust (soft-wood)	33		3.0		.6		10			
Olive stones from Spain	35		4.0		1.2		4			

Meiler process yields; percentage by volume:

Beech; smooth split billets, 150 mm. diameter up	64
Oak; smooth split billets, 150 mm. diameter up	66
Oak; branchwood, 50-150 mm. diameter	42
Spruce; split billets	78
Spruce; roots and stumps	68
Spruce; poles, 50-150 mm. diameter	58
Spruce; mixed	72
Spruce; branchwood	46

One cubic meter of solid charcoal is the result of the carbonization of about 190 kg. of birch wood, or 148 kg. of

spruce by pit method; and from 131 kg. of silver fir by the retort process. There is practically no difference in actual specific gravity between the various charcoals resulting from different woods, but apparent density determinations give a figure of 0.4 for birch charcoal, 0.27 for spruce charcoal, and 0.22 for silver fir charcoal.

The carbon exists in charcoal as solid carbon, volatile carbon, and carbon produced by absorption of hydrocarbons during cooling. Due to the great rapidity with which charcoal absorbs gases, it has not been possible to prepare a charcoal entirely free of volatile matter. It is very likely that the most fully carbonized charcoal is really a compound of carbon and hydrogen. Approximate analyses of charcoals from various sources are given below. The meiler charcoal shows the highest carbon content while the retort charcoal shows the highest percentage of absorbed gases:

Source	% C	% H	O ₂ + N ₂	% Ash	Final temp. of Carbonization° C
Meilers.....	90.36	3.74	5.72	1.1	above 600° C
Kilns (with admission of air)	84.18	3.32	11.72	.78	500
Retorts (with no air).....	81.15	4.24	13.64	.97	350

The calorific value of meiler charcoal is approximately 7,900 kg. calories per kg.; of kiln charcoal, 7,350 kg. calories per kg.; and of retort charcoal, 7,300.

In measurements on the porosities of charcoal, Juon¹ found considerable variation depending upon the original raw material and the method of manufacture. The pores, or voids, in charcoal will constitute from 70 to 85% of its total bulk, the solids varying from 15 to 30%. The capacity of charcoal to absorb gases and vapors, to float on water, and to ignite spontaneously, are functions of its porosity.

Charcoal, after being cooled in the absence of air, subsequently increases in weight owing to the absorption of

¹ Stahl und Eisen, vol. 24, p. 1230 (1904).

gases and more especially water vapor. The extent of this increase differs for different kinds, and is dependent upon climatic conditions. Ordinarily, equilibrium is reached in about three weeks with an 80% increase in weight. About one half of this increase was added during the first 72 hours after the charcoal was made.

In thickly wooded countries, charcoal is used industrially only as fuel. The product formerly produced entirely in meilers was employed on a large scale in iron and steel metallurgy. In this use it has largely been displaced by coke, but in the Urals, Hungary and Sweden it still finds large application for making charcoal iron. More than 90% of Sweden's consumption is produced in meilers. Charcoal still finds considerable application as a kitchen fuel, in bakers' ovens, in open braziers, in crucible furnaces in which silver, copper and the precious metals are melted, in brass forging furnaces, and in other applications where a hot fire without smoke is required. Considerable tonnages of charcoal are still consumed in the manufacture of certain kinds of gunpowder and blasting explosives. Charcoal is characterized externally by retaining the form and structure of the wood from which it was produced. The shape of the bark, the annual rings on the transverse sections, the fibrous structure of the longitudinal sections of the original wood are all clearly preserved in the finished charcoal. These characteristics afford means of determining the origin of the product. A charcoal, to be of satisfactory commercial quality, must have the following properties: a black and glistening appearance with a distinct blue tinge; the production of a metallic note when struck on a hard object; a freedom from taste or smell; of such physical form that when touched to the tongue small particles of the charcoal will adhere to the surface of the tongue; when broken transversely, the freshly exposed surface can be rubbed without soiling the fingers. The charcoal must be capable of easy ignition and must burn quietly without smoke or flame.

A dense wood with narrow annual rings gives a dense

charcoal, while a rotten, porous wood will usually produce a weak and easily friable product. Cracks in the main body of the charcoal usually run in the direction of the transverse fibres and seldom in that of the longitudinal fibres. Charcoal from wood of small diameter, such as poles or branches, exhibits fewer cracks than charcoal from trunk wood.

It has been found by experience that for the production of a material which is not only black but possesses the remaining characteristic properties, the final temperature measured in the interior of the carbonizing apparatus must be at least 375° C. Charcoal produced below 300° appears red or has a reddish tinge. At one time this quality of charcoal was demanded for gunpowder manufacture and smelting purposes. Under certain climatic conditions, such as extreme dryness, even high grade charcoal may assume a reddish tinge. Color, therefore, is not always a safe quality standard.

On an economic basis the charcoal made must at least cover the cost of the wood carbonized. The selling weight of charcoal is ordinarily taken as 107% of the weight obtained directly after cooling. "Smalls" and "breeze" amounting to from 3 to 6% are deducted and lost in screening.

In some countries, peat charcoal is made as a means of providing fairly satisfactory fuel from an otherwise waste product. Peat may be economically charred by means of waste gases of smelting furnaces or of heated gases produced by the combustion of wood. Peat charcoal is very friable, having little compressive strength, and is usually unsuited for metallurgical operations. It has a high ash content amounting in some cases to almost one half the weight of the charcoal. Much of the equipment used in carbonizing wood has at one time or another been experimentally used for making peat charcoal. The total tonnage of peat charcoal produced in the world is very small in comparison to that of wood charcoal.

CHAPTER XVI

GAS ADSORBENT CHARCOAL

THE World War brought into existence, as an article of commerce, a new product known as "activated" carbon. It originated as a means of defense against toxic gases in warfare. It is rapidly finding industrial applications, the extent and novelty of which are as yet not generally appreciated.

The power of wood charcoal to remove odors by adsorption has been known for many years. In the form of wood ashes, charcoal has been employed for decades, in outhouses and elsewhere to eliminate unpleasant odors. Shenstone¹ in 1854 invented a respirator filled with powdered wood charcoal to be worn in hospitals. It was to adsorb and then destroy germs of cholera and other diseases. This was the forerunner of the modern gas mask. It is not known whether the oxidizing action of the charcoal is due to anything more than the increase in concentration of the oxygen. Ray and Chaney² advocate the use of activated carbon for removing and abating industrial stenches.

More than a half century ago, Hunter³ showed that many different gases and vapors are adsorbed by charcoal to a marked extent. His experiments cover more ground than those of anyone else, although they are probably not very accurate and are not made at comparable temperatures and pressures. Hunter expressed the adsorption in volumes of gas adsorbed per volume of charcoal. Some of his results are given in Table XII.

¹ Pharm. J., vol. 13, p. 454 (1854).

² Chem. & Met. Eng., vol. 29, p. 359 (1923).

³ Phil. Mag. (4), vol. 25, p. 364 (1863); J. Chem. Soc., vol. 18, p. 285 (1865); vol. 20, p. 160 (1867); vol. 21, p. 186 (1868); vol. 23, p. 73 (1870); vol. 24, p. 76 (1871); and vol. 25, p. 649, (1872).

TABLE XII

ADSORPTION OF GASES AND VAPORS BY COCONUT CHARCOAL
Volumes of Gas adsorbed per volume of charcoal.

Gas	Volume	Temp. ° C.	Pressure mm./Hg.
Acetic acid	83	159	676
Water	24	159	24
Water	44	128	624
Benzene	59	130	646
Ethyl alcohol	84	160	663
Ethyl alcohol	111	127	644
Ethyl alcohol	141	100	652
Ethyl acetate	72	154	659
Carbon tetrachloride	4	155	695
Carbon tetrachloride	8	100	636
Methyl alcohol	61	159	684
Methyl alcohol	127	129	663
Methyl alcohol	151	100	652
Chloroform	21	159	660
Chloroform	30	100	651
Acetone	68	157	671
Acetone	105	100	642
Carbon bisulphide	91	158	659
Carbon bisulphide	117	100	671
Ethyl ether	54	160	684
Ethyl ether	68	128	661
Ethyl ether	87	100	644
Acetaldehyde	67	155	687
Acetaldehyde	139	100	681
Ammonia	22	127	655
Ammonia	83	70	760
Ammonia	88	60	760
Ammonia	114	40	760
Ammonia	96	50	760
Ammonia	149	20	760
Ammonia	176	0	760
Cyanogen	87	70	760
Cyanogen	92	60	760
Cyanogen	96	50	760
Cyanogen	99	40	760
Cyanogen	107	20	760
Cyanogen	114	0	760
Hydrochloric acid	60	100	668
Nitrous oxide	64	100	661
Carbon dioxide	17	127	687
Carbon dioxide	71	0	760
Nitrogen	15	3	760
Hydrogen	4	3	760

Dewar⁴ measured the adsorption of argon, helium and some more common gases in coconut char at low temperatures. The volumes absorbed, as given in Table XIII have been calculated back to 0° C. and 760 mm. pressure.

TABLE XIII

ADSORPTION OF GASES BY COCONUT CHARCOAL
Volumes of gas adsorbed per volume of charcoal.

Gas	Volume	Temp. ° C.
Argon	12	0
Argon	175	-185
Oxygen	18	0
Oxygen	230	-185
Carbon monoxide	21	0
Carbon monoxide	190	-185
Nitrogen	15	0
Nitrogen	155	-185
Hydrogen	4	0
Hydrogen	135	-185
Helium	2	0
Helium	15	-185

TABLE XIV

Amts. Exposed to Charcoal	Residue Pumped off
8.50 cc.	8.36 cc.
18.42	18.32
18.52	18.37
29.58	29.44
34.97	34.73
41.69	41.40
41.98	41.87

McLean⁵ found that a very small amount of helium was adsorbed by charcoal at the temperatures of liquid air. He admitted various amounts of helium to a special apparatus charged with 30 g. of charcoal cooled to liquid air temperature where the gas was allowed to remain for 30 minutes.

⁴ Proc. Roy. Soc., vol. 74, p. 124 (1924).

⁵ Trans. Roy. Soc. Canada, vol. 12 (III) pp. 79-81 (1918).

Unadsorbed residues were pumped out and measured. The table gives the amounts exposed to the charcoal and the corresponding amounts of gases pumped off. Only a very small amount of helium was retained by the charcoal.

As a first approximation it is often stated that the higher the boiling point of a gas or vapor, the more readily is it adsorbed by charcoal. A table of boiling points of some of the substances whose adsorption by charcoal was studied is given in Table XV. Thus helium is taken up by charcoal much less than hydrogen, and hydrogen to a lesser extent than nitrogen or oxygen. Carbon dioxide is adsorbed less readily than ammonia, so that these substances follow the experimental rule. Nitrogen, however, is adsorbed more readily than argon, while both argon and oxygen are adsorbed to a lesser extent at 0° than carbon monoxide, which according to the rule, should not be so. Claude⁶ has shown as a result of his study of the adsorbing power of charcoal for helium, neon and hydrogen at the temperature of liquid nitrogen (-195.5°), and of nitrogen at the temperature of liquid oxygen (-182.5°), that the adsorption of hydrogen did not follow the rule that the more easily liquefiable gases were the more readily adsorbed, although the other gases did. Nitrous oxide is less strongly adsorbed than ethylene, and nitric oxide more than methane, which is not according to the boiling points. Although carbon dioxide is more readily condensable than ethane, ethylene and acetylene, these three gases are adsorbed to a greater extent at 20° than is carbon dioxide. The empirical rule of adsorption according to boiling points has too many exceptions. Hydrogen sulphide is adsorbed more than ammonia, which same is true also for chlorine. Cyanogen is adsorbed more than ammonia at 70° and less at 0° . There is no relation between boiling points and amounts of adsorption in the case of vapors. Going from lower to higher boiling points, we have the order: aldehyde, ether, chloroform, methyl alcohol,

⁶ Compt. rend., vol. 158, pp. 61-4.

TABLE XV.
BOILING POINTS OF VARIOUS LIQUIDS

Liquid	B. Pt. (deg. C.)	Liquid	B. Pt. (deg. C.)
He	—268.7	Cl ₂	— 33.7
H ₂	—252.6	NH ₃	— 33.5
N ₂	—195.7	(CN) ₂	— 21
CO	—190	SO ₂	— 10
A	—186.1		
O ₂	—182.8	CH ₃ CHO	+ 20.8
CH ₄	—164	(C ₂ H ₅) ₂ O	+ 34.6
NO	—153	CS ₂	+ 46.2
C ₂ H ₄	—105	Br ₂	+ 58.6
N ₂ O	— 89.8	CHCl ₃	+ 61.2
C ₂ H ₆	— 84.	CH ₃ OH	+ 64.7
HCl	— 82.9	CCl ₄	+ 76.7
C ₂ H ₂	— 82.4 ⁷	C ₂ H ₅ OH	+ 78.4
CO ₂	— 79 ⁷	C ₆ H ₆	+ 80.2
H ₂ S	— 60.2	H ₂ O	+ 100.0

carbon tetrachloride, ethyl alcohol, benzene and water. The order of increasing adsorption is carbon tetrachloride, chloroform, water, benzene, ether, aldehyde, ethyl alcohol, and methyl alcohol. From the experiments of Lemon and Blodgett,⁸ Wilson⁹ concludes that the nitrogen and oxygen adsorption by charcoal is very nearly in the inverse ratio of their molecular volumes. Lamb and Coolidge¹⁰ find a similar relation for the adsorption of carbon tetrachloride, ether, methyl alcohol and the vapors of a number of other substances. Richardson and Woodhouse¹¹ find this to be true for the adsorption of nitrous oxide and carbon dioxide only within the pressure range varying from 180 to 280 cm. Bancroft¹² expresses the opinion that the truth of the mat-

⁷ Sublimation point.

⁸ Phys. Rev. (2) vol. 14, p. 394 (1919).

⁹ Phys. Rev. (2) vol. 16, p. 8 (1920).

¹⁰ J. Am. Chem. Soc., vol. 42, p. 146 (1920).

¹¹ Jour. Am. Chem. Soc., vol. 45, p. 2650 (1923).

¹² Applied Colloid Chemistry — McGraw-Hill Book Co.

ter is obtained when we consider that adsorption is specific and varies with the nature of both the gas and the adsorbing solid. Charcoals differ widely among themselves. For comparative purposes only there is given in Table XVI Hunter's results on charcoals made from different woods. The coconut charcoal has the greatest adsorbing power of all.

TABLE XVI

ADSORPTION OF GASES BY CHARCOAL FROM DIFFERENT WOODS
Volumes of gas per volume of charcoal.

Wood	Volume Ammonia	Volume CO_2	Volume $(CN)_2$
Logwood	111	55	87
Ebony	107	47	90
Camwood	91	45	
Green ebony	90	41	
Fustic (Cuba)	90	58	
Lignum vitae	89	47	
Boxwood	86	31	29
Jamaica logwood	69	33	
Sapan wood	70	32	
Beech	58		
Rosewood	51		
Wistaria sinensis	44		
Vegetable ivory		50	57
Coconut shell	176	71	114

Logwood charcoal shows the greatest action on ammonia and the charcoal from fustic on carbon dioxide, while ebony charcoal shows the greatest adsorption of cyanogen. The most porous charcoal in the ordinary sense does not adsorb the most gas. This can readily be seen when it is considered that charcoal made from the shell of the coconut is very dense and brittle. When the charcoal is broken, the fractured surfaces show a semi-metallic lustre. The pores are quite invisible. It has been suggested many times that the best adsorbers are charcoals with very many pores of very small diameter, because they will then present the largest surface for condensation. There are, however, other factors besides the extent of surface. One of the most important of these is the arrangement of the surfaces. Two plain

surfaces placed close to each other will apparently adsorb a great deal more gas than the same surfaces would if each did not reinforce the other and modify the concentration gradient. Adsorption also depends on the structure of the adsorbent. Down to a certain limit, from a theoretical standpoint narrow pores should adsorb greater quantities than those of spherical shape. This is actually true. Cleanliness of the adsorbing surface is absolutely essential. While there may be an actual difference in the amount of surface, the presence of substances in the charcoal which affect the adsorption adds another factor. Charcoal is far from being pure carbon. The great improvements in the manufacture of gas mask charcoal have been along the line of cleaning the charcoal surfaces as well as increasing the surfaces. The so-called activation of coconut charcoal by heating with steam at 950° removed hydrocarbons which interfered with gaseous adsorption and also developed more pores. Burning out some of the carbon increased the porosity of the available surface up to a certain point, beyond which the mass of active carbon per unit of surface falls off so much that the adsorption decreases.

Because it is the best all-round adsorbent for toxic gases, charcoal is used almost universally in most gas masks. Its manufacture and activation will be discussed more completely later on in this chapter. The removal of toxic materials must be complete to a very minute degree. Within the tenth of a second that the air takes in passing through the canister of a gas mask, the adsorbent must be capable of reducing the toxic gas concentration from approximately 100 parts per million by volume to 1 p.p.m. or less. A good gas mask charcoal will reduce the concentration of 7,000 p.p.m. of chloropicrin in a rapidly moving current of air in less than .3 second to .5 p.p.m. The use of adsorbent charcoal is extending very rapidly both in commercial and experimental work. An interesting application is shown by the work of Melsens who placed wood charcoal saturated with dry chlorine in the longer branch of a bent sealed tube,

dipped that end of the tube into boiling water while the shorter branch was placed in a freezing mixture. The pressure which developed when a portion of the gas was volatilized caused liquefied chlorine to appear in the cold portion of the tube. Cyanogen, sulphur dioxide, hydrogen sulphide and hydrogen bromide can be liquefied in this way, but bromine, hydrogen chloride, carbon bisulphide, ether and alcohol can not.

The use of charcoal as a means of obtaining a high vacuum was described by Tait and Dewar ¹³ in 1874. They placed a piece of charcoal in a tube having platinum electrodes, heated the tube to a red heat and sealed it after exhaustion with a Sprengel pump. If the tube were cool, no spark would pass when using an induction coil capable of giving a $\frac{1}{4}$ in. spark. When the tube was heated, enough gas was given off from the charcoal to allow the spark to pass. Dewar ¹⁴ obtained surprising results by making use of the increased adsorption of charcoal at low temperatures. He connected a 300-cc bulb containing air at 15° and a pressure of 1.7 mm. with another bulb holding 5 g. of charcoal. When the charcoal was cooled in liquid air the pressure dropped to .00005 mm. In other experiments he connected a Crookes radiometer tube filled with hydrogen at atmospheric pressure to a charcoal bulb. When the charcoal bulb was subjected to liquid air temperatures, no rotation took place even when the beam from an electric arc was focussed on the vanes of the radiometer. The motion became quite rapid, however, when the charcoal bulb was placed in liquid hydrogen. The adsorption of helium by charcoal at -252° is not enough to make this experiment successful when the radiometer tube is filled with helium.

Ramsay ¹⁵ used Dewar's method of employing cooled coconut charcoal as an adsorbent for gases to determine the amount of neon and helium in the air. At -100° oxygen,

¹³ Proc. Roy. Soc. Edin., vol. 8, p. 348 and 628 (1874).

¹⁴ Proc. Roy. Inst., vol. 18, pp. 437 and 756 (1906).

¹⁵ Proc. Roy. Soc., vol. 76A, p. 111 (1905); vol. 80A, p. 599 (1906).

argon and nitrogen are removed quantitatively while the neon and helium adsorption is negligible. At -185° practically all of the neon is adsorbed and none of the helium. Woodrow¹⁶ obtained pressures as low as 2×10^{-7} mm. by the use of activated charcoal for adsorbing gases.

A very effective lecture experiment based on the selective adsorption of charcoal has been worked out by Dewar.¹⁷ A train of spectroscopic tubes which includes a U-tube containing charcoal are exhausted by cooling the charcoal until the electric discharge will barely pass. The charcoal tube is now placed in liquid air and air allowed to enter the system slowly, passing first through the charcoal tube which removes the readily adsorbed gases such as oxygen, nitrogen and argon, while helium, neon and hydrogen pass through. The first tube soon begins to glow with the well-known rich orange hue of neon when the pressure in this tube has risen sufficiently. In time the characteristic discharges of neon and helium appear in the other tubes.

Krypton and xenon may be obtained from air by means of cooled charcoal. Air is passed through a series of tubes immersed in liquid air for the purpose of purification, the last tube containing cotton wool to filter out dust and solid particles. The pure air is then passed through a tube containing about 100 g. of charcoal for at least 24 hours. The tube is then removed from the train and placed in solid carbon dioxide, and the gases which are evolved allowed to escape. The gas remaining in the charcoal at -78° is driven off by heating and exhaustion, the carbon compounds and oxygen being removed from it. The remaining gases, consisting of nitrogen, krypton and xenon, are condensed and fractionated. The spectrum tubes of krypton and xenon may be readily prepared by stirring charcoal in liquid air and allowing the latter to evaporate. The gases remaining in the charcoal can then be separated as before. Moore¹⁸

¹⁶ Phys. Rev. (2) vol. 4, p. 491 (1914).

¹⁷ Proc. Roy. Inst., vol. 18, p. 444 (1906).

¹⁸ J. Frank. Inst., vol. 191, p. 184 (1921).

uses charcoal in the final purification of the commercial preparation of helium for aircraft use. Burrell¹⁹ and his co-workers have developed commercial methods for the recovery of gasoline from natural gas using adsorbent charcoal, ordinarily the coconut shell type. Urbain has employed charcoals made from peat for this same type of work. These will be described in greater detail later on in the chapter.

When mixtures of gases, such as nitrogen and oxygen, are adsorbed by charcoal, the results may be complicated by an oxidation of the carbon. Dewar²⁰ found that the mean composition of air adsorbed by charcoal at -185° was about 56% oxygen. This evidently shows a selective adsorption of oxygen. When this was allowed to distill over slowly, the first liter out of six showed 18.5% oxygen, the second 20.6, the third 53.0, the fourth 72, the fifth 79, and the sixth 84% oxygen. In some other experiments by Dewar, oxygen adsorbed at -185° was apparently given off at $+15^{\circ}$ without any appreciable contamination by the oxides of carbon. The results are quite different at higher temperatures, presumably due to the removal of oxygen by combustion.²¹

Lowry and Hulett²² found that charcoal slowly reacts with oxygen at ordinary temperatures. There appears to be formed a solid oxide of carbon which, when heated, breaks down into mixtures of carbon dioxide, carbon monoxide and carbon. The amounts of oxygen thus fixed varied from 1.7 to 3.8% of the weight of the charcoal.

¹⁹ "Recovery of Gasoline from Natural Gas." New York, Chemical Catalog Co.

²⁰ Proc. Roy. Soc., vol. 74, p. 126 (1904); Proc. Roy. Inst., vol. 18, p. 184 (1905).

²¹ Skey: Chem. News, vol. 15, p. 15, 27 (1867); Storey and Lewis: Am. Chem. J., vol. 4, p. 409 (1883); Blumtritt: J. prakt. Chem., vol. 98, p. 418 (1886); Baker: J. Chem. Soc., vol. 51, p. 249 (1887); Craig: Chem. News, vol. 90, p. 109 (1904); Rhead and Wheeler: J. Chem. Soc., vol. 51, p. 249 (1887).

²² J. Am. Chem. Soc., vol. 42, p. 1408 (1920).

When a slowly dying wood fire is blown on by means of a bellows, the fire will often start burning again quite briskly. This is in spite of the fact that the large influx of cooler air must tend to chill the embers and thus to put out the fire. Bacon²³ suggests that the dying embers are covered with an adsorbed film of carbon dioxide which is swept away to some extent by the draft of the bellows. There is less carbon dioxide adsorbed at the higher temperature when the fire is burning briskly. The natural draft is then sufficient to bring oxygen to the burning wood. This hypothesis is more probable when the experiments of Arndt and Schraube²⁴ are considered. They found that even at red heat carbon dioxide is adsorbed more strongly by charcoal than carbon monoxide or nitrogen.

When mixtures of gases are adsorbed, it seems to be the general rule that the one more readily adsorbed displaces the other to some extent and is itself adsorbed to a relatively greater amount than one would have predicted from the experiments on single gases. Magnus and Roth²⁵ in their study of adsorption of carbon dioxide and hydrogen by wood charcoal found that the hydrogen adsorption at any temperature was proportional to its partial pressure, but only at the higher temperatures for the range of 0° to 148° was the carbon dioxide adsorption proportional to the partial pressure of carbon dioxide. Bergter²⁶ found that oxygen at pressures of 0.5 to 10 mm. is adsorbed 30 to 40 times as strongly as nitrogen, and that at these pressures the presence of oxygen increases the amount of nitrogen adsorbed. With readily condensable gases, the vapors of one may help to cause the vapors of another to be adsorbed. Hunter²⁷ studied the striking instance of water and ammonia. It seems probable, however, that the adsorbed water dissolves

²³ J. Phys. Chem., vol. 17, p. 768 (1913).

²⁴ Nernst Festschrift, vol. 46 (1912).

²⁵ Z. Anorg. Allgem. Chem., vol. 150, p. 311-25 (1926).

²⁶ Ann. Phys. (4) vol. 37, p. 480 (1902).

²⁷ J. Chem. Soc., vol. 23, p. 73 (1870).

or adsorbs ammonia, thus increasing the amount of ammonia apparently held by the charcoal. Work on gas mask carbon has shown that traces of benzene or ether will increase the service time of charcoal against chlorpicrin.

Matwin²⁸ states that charcoal is an excellent adsorbent for carbon bisulphide and carbonyl sulphide in illuminating gas. Lorenz and Wiedbrauck²⁹ find that in adsorption from mixtures of carbon dioxide and hydrogen with increase in the carbon dioxide content of the gas, the time necessary to reach equilibrium decreases and the amount of gas necessary to saturate the charcoal increases. They state that the increase in total adsorbed gas is due to the high adsorption of carbon dioxide. They show that hydrogen is more difficult to adsorb than carbon dioxide. The temperature effect is small. They obtained similar results with carbon dioxide-carbon monoxide mixtures. In this case the gas content of the adsorbent increases more rapidly than was the case with carbon dioxide-hydrogen mixtures. With carbon dioxide-ethylene mixtures, the adsorption increase with increasing carbon dioxide content is much greater, but the relative carbon dioxide content of the gas is increased and that in the adsorbent decreased. Ethylene is more readily adsorbed than carbon dioxide. The equilibrium curve varies considerably from that of either carbon dioxide or the mixture. Carbon monoxide adsorption is almost identical with that of carbon dioxide-ethylene. Comparison of carbon monoxide and carbon dioxide-carbon monoxide shows that adsorption of the more readily adsorbable gas is greatly diminished by the presence of the more difficultly adsorbed gas in the adsorbent. At low pressures adsorption of ethylene is greater than that of carbon dioxide, while this condition is reversed at higher pressures. Lorenz explains this according to the Langmuir theory as due to adsorption of the unsaturated hydrocarbon by secondary valences at lower pressures, which valences are saturated at higher pressures.

²⁸ Jour. Gasbeleuchtung, vol. 52, p. 602 (1909).

²⁹ Zeit. Anorg. Allgem. Chem. vol. 143, pp. 68-76 (1925).

All the results of Lorenz were obtained from charcoal of the same batch.

Wilson³⁰ shows that Lemon and Blodgett's³¹ data for the adsorption of mixtures of oxygen and nitrogen can be calculated if the assumption is made that 1 gram molecular weight of nitrogen is equivalent in every way to 1.39 gram molecular weights of oxygen. The adsorption of nitrogen by charcoal at a pressure of 80 atmospheres was shown by Briggs³² to be cut down from 100 cc. per cc. of charcoal to about 56 cc. when the charcoal had previously taken up 25% of moisture. Richardson and Woodhouse³³ found that neither carbon dioxide nor nitrous oxide has any effect on the adsorption of the other by charcoal.

In the cases of marked adsorption of gases by charcoal, the determination of the probable density of the adsorbed gas is of interest. A calculation by Mitscherlich³⁴ showed that when carbon dioxide at 12° and atmospheric pressure is adsorbed by boxwood charcoal, the carbon dioxide occupies only one fifty-sixth of its original volume. It is usually assumed that some of the gas has been liquefied inasmuch as this volume is a lesser one than the same amount of carbon dioxide can occupy as a gas at any temperature. It is, however, possible to consider the carbon dioxide as being present in the form of a non-liquefied, highly condensed gas. The magnitude of the heat of adsorption when charcoal adsorbs carbon dioxide is in favor of the theory that part or all of the carbon dioxide has been liquefied. Dewar³⁵ calculated the apparent density of some gases adsorbed by coconut charcoal at low temperatures. The data given in Table XVII are of the same order as those of the liquid gases, in some cases being even greater than this.

³⁰ Phys. Rev. (2) vol. 16, p. 8 (1921).

³¹ Phys. Rev. (2) vol. 14, p. 394 (1919).

³² Trans. Roy. Soc. Edin., vol. 41, p. 121 (1921).

³³ J. Am. Chem. Soc., vol. 45, p. 2638 (1923).

³⁴ Sitzungsber. Akad. Wiss. Berlin, 1841, p. 376.

³⁵ Proc. Roy. Inst., vol. 18, p. 438 (1906).

TABLE XVII
DENSITY OF GASES ADSORBED BY CHARCOAL
Density in grams per cubic centimeter.

Gas Adsorbed	Temperature of Adsorption	Density of Adsorbed Gas	Density of Liquefied Gas
Carbon dioxide	+15	0.70	0.80
Oxygen	-183	1.33	1.12
Nitrogen	-193	1.00	0.84
Hydrogen	-193	0.06	0.07
Hydrogen	-210	0.08	
Hydrogen	-252	0.11	
Helium	-258	0.17	(0.122)

Because of this extreme condensation of the gas, a nitrogen cylinder filled with dry coconut charcoal has been shown by Briggs³⁶ will discharge 66% more nitrogen when the pressure drops from 35 atmospheres to 1 than will a similar cylinder containing no charcoal. Bancroft³⁷ gives the molecular heats of adsorption and liquefaction of gases when adsorbed by charcoal as shown in Table XVIII.

TABLE XVIII
MOLECULAR HEATS OF ADSORPTION AND OF LIQUEFACTION
OF GASES

Adsorbing Agent	Gas	Adsorption g. cal. per mol.	Liquefaction g. cal. per mol.
Charcoal	NH ₃	5,900—8,500	
Charcoal	CO ₂	6,800—7,800	6,250
Charcoal	N ₂ O	7,100—7,700	4,400
Charcoal	SO ₂	10,000—10,900	5,600
Charcoal	HCl	9,200—10,200	
Charcoal	HBr	15,200—15,800	
Charcoal	HI	21,000—23,000	
Charcoal (-185°)	H ₂	1,600	238
Charcoal (-185°)	N ₂	3,686	1,372
Charcoal (-185°)	Ar	3,636	
Charcoal (-185°)	O ₂	3,744	1,664
Charcoal (-185°)	CO	3,416	

³⁶ Proc. Roy. Soc. Edin., vol. 41, p. 122 (1921).

³⁷ W. D. Bancroft: Applied Colloid Chemistry, p. 27

Melsens³⁸ found that when different liquids were added to freshly ignited wood charcoal, there was a temperature rise with ether, alcohol and carbon bisulphide. This was true to a greater extent in the case of bromine, which produced a 30° rise when 97 g. of bromine were added to 11 g. of charcoal. Since a sudden compression of 10 atmospheres raises the temperature of water only one seventy-seventh of a degree, Melsens concluded that a rise of temperature of 1.16 when charcoal was wetted by water corresponds to a pressure of 893 atmospheres. From calculations made in the same manner, he estimated that the force of adsorption of charcoal for bromine is 3,100 atmospheres, 13,090 for carbon bisulphide, 4,620 for ether and 3,080 for alcohol.

Studies in the heat evolution on wetting charcoal with various materials have been made by Gaudechon.³⁹ The values are given in the Table XIX.

Lamb and Coolidge⁴⁰ find that curves are obtained when the heats of adsorption of the vapors of some organic liquids by charcoal are plotted against the amounts adsorbed. These curves approximate straight lines. They term the difference between the heat of adsorption and the heat of vaporization the net heat of adsorption. This is practically constant for the different liquids studied, when referred to equal volumes of adsorbed liquid. If it be assumed that this net heat of adsorption is a heat of compression, the attracting force when 1 cc. of liquid is adsorbed by 10 g. of charcoal may be estimated to be about 37,000 atmospheres.

For the sake of completeness, we will include in this discussion some adsorption isotherms for charcoal and various gases. The adsorption isotherm is the curve obtained when the amounts of adsorbed gases are plotted against the pressures in any system. From his measurements with hydrogen adsorbed by charcoal at -185°, Dewar⁴¹ states that the

³⁸ Ann. Chim. Phys. (5) vol. 3, p. 522 (1874).

³⁹ Comptes rendus, vol. 157, p. 209 (1913).

⁴⁰ J. Am. Chem. Soc., vol. 42, p. 1146 (1920).

⁴¹ Proc. Roy. Inst., vol. 18, p. 437 (1906).

TABLE XIX
HEAT EVOLUTION ON WETTING
Gram calories per gram adsorbent

	<i>Charcoal</i>
Water	3.9
Methyl alcohol	11.5
Ethyl alcohol	6.9
Propyl alcohol	5.6
Amyl alcohol	3.7
Formic acid	12.0
Acetic acid	6.0
Acetone	3.6
Chloroform	2.3
Ether	1.2
Benzene	4.2
Carbon tetrachloride	1.5
Carbon bisulphide	4.0

amount adsorbed is seen to increase with the pressure up to 10 atmospheres, after which the phenomenon seems to be independent of the pressure. At the temperature of liquid air, 6.7 g. of charcoal would not adsorb more than about 1 liter of hydrogen, even though the pressure were raised from 10 to 25 atmospheres. A large number of studies of the quantitative variation of the adsorption by charcoal with the pressure have been made.⁴² The adsorption curve for hydrogen in charcoal as determined by Titoff⁴³ is given in Fig. 35, and the data for charcoal as given by Richardson⁴⁴ at various temperatures is given in Fig. 36. The data for carbon dioxide as obtained by Geddes⁴⁵ is given in Fig.

⁴² Travers: Proc. Roy. Soc., vol. 78A, p. 9 (1906); Davis: J. Chem. Soc., vol. 91, p. 1066 (1907); Geddes: Ann. Physik. (4), vol. 29, p. 797 (1907); Boyle: J. Phys. Chem., vol. 12, p. 484 (1908); Phil. Mag. (6), vol. 17, p. 377 (1909); McBain: vol. 18, p. 916 (1909); Z. Physik. Chem., vol. 68, p. 471 (1909); Homfray: vol. 74, p. 139, 687 (1910); Titoff: vol. 74, p. 641 (1910); Piutti and Maglia: Gazz. chim. ital., vol. 40, I, p. 569 (1910).

⁴³ Z. Phys. Chem., vol. 74, p. 641 (1910).

⁴⁴ J. Am. Chem. Soc., vol. 38, p. 1828 (1917).

⁴⁵ Ann. Physik. (4), vol. 29, 797 (1909).

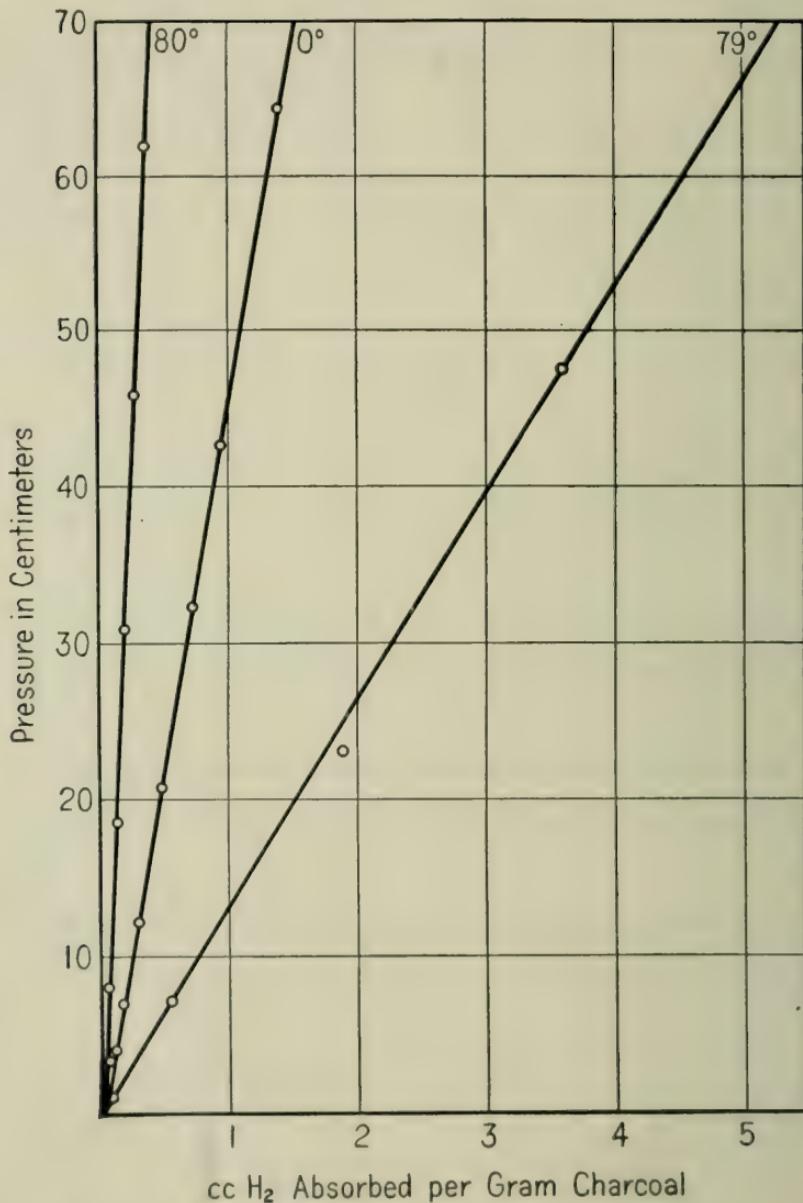


FIG. 35.—ADSORPTION CURVE FOR HYDROGEN BY CHARCOAL

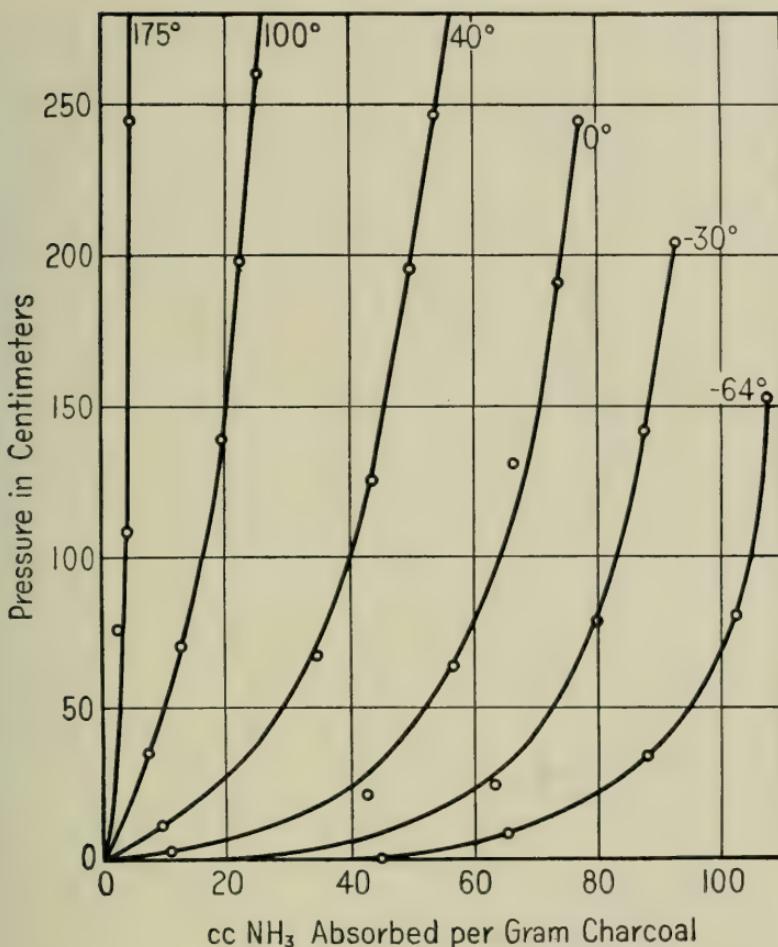


FIG. 36.—ADSORPTION OF AMMONIA AT VARIOUS TEMPERATURES BY CHARCOAL

37. Hinteler⁴⁶ finds that the Freundlich equation $(x/m)^n = Kp$, where x is the amount of gas adsorbed, m the amount of adsorbing solid, p the pressure and K and n are empirical constants determined for each temperature, holds for vapors of hexane, benzene, carbon bisulphide, chloroform, acetone, ethyl alcohol, methyl alcohol and water when adsorbed by charcoal.

⁴⁶ Z. Phys. Chem., vol. 91, p. 103 (1916).

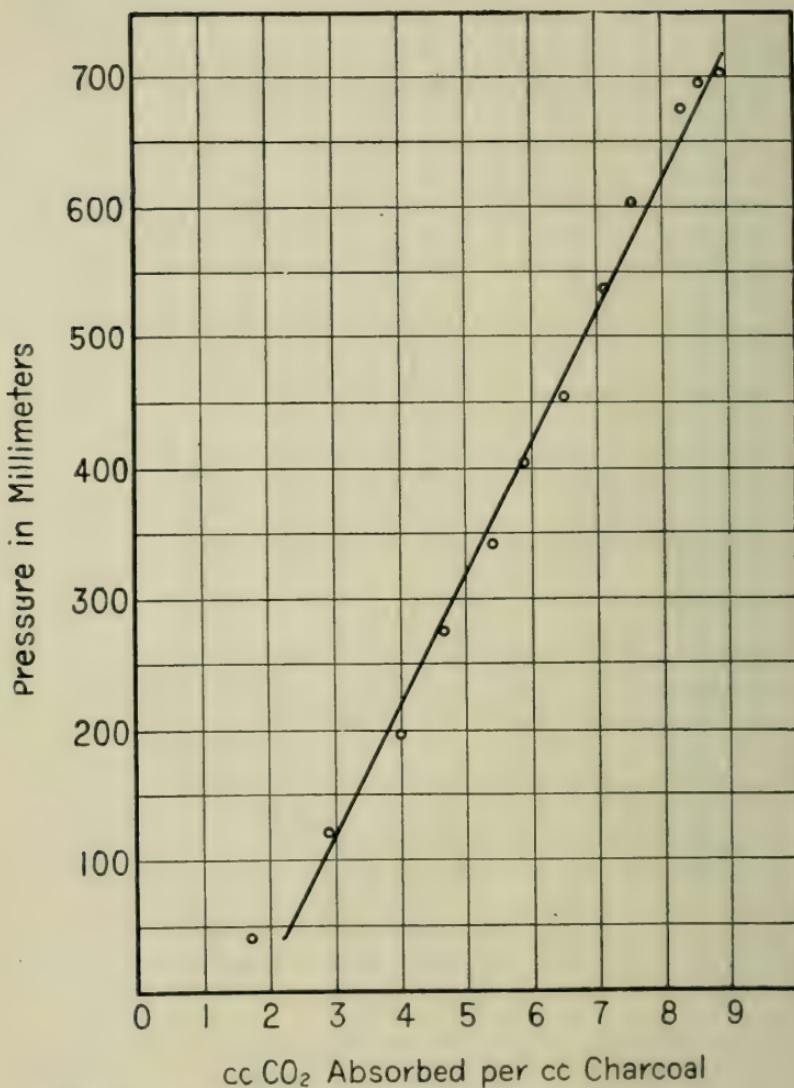


FIG. 37.—ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

The amount of adsorption by charcoal varies with the surface and the extent of this surface. The change produced by grinding the charcoal is very slight, because the original surface of the unground charcoal is so enormous. It is esti-

mated by Lagergren⁴⁷ that 1 g. of charcoal has a surface of 4 square meters and is composed of about 1.4 billion particles. Lamb, Wilson and Chaney⁴⁸ considered that 1 cubic centimeter of active gas mask charcoal has a surface of 1,000 sq. meters at the most effective density, 0.4.

Many theories have been proposed to explain the mechanism of adsorption. For these the reader is referred to other works.

Experimental work over a considerable range has shown that when free carbon is liberated from its compounds below approximately 600° to 700° C. by carbonization, it was either active or else capable of activation, while carbon produced at temperatures higher than this was ordinarily shown to be inactive and not capable of activation. Chaney proposes, therefore, that activated carbon is essentially a special form of amorphous carbon deposited at low temperatures and free from adsorbed and stabilized hydrocarbons which are normally associated with it. These hydrocarbons lessen its power to combine with or adsorb other substances. Activated carbon is also stated to be free from inactive carbon on its surface, which carbon was formed by the decomposition of hydrocarbons at high temperatures. Primary carbons of the amorphous variety are assumed to consist essentially of a stabilized complex of hydrocarbons adsorbed on a base of active carbon. These primary carbons do not possess high specific adsorptive power inasmuch as the active carbon has been saturated by the hydrocarbon adsorbed on it.

A gas-adsorbent charcoal, particularly for military purposes and almost to the same extent for industrial purposes, carries a heavy premium when the maximum of adsorptive capacity is obtained per unit volume of adsorbent. A number of commercial decolorizing chars are stated to have on an equivalent weight basis the same gas-adsorbing properties as the better grade of carbon made especially for this

⁴⁷ Van Bemmelen: "Die Absorption," p. 410 (1910).

⁴⁸ J. Ind. Eng. Chem., vol. 11, p. 420 (1919).

purpose. There exists a definite critical density or porosity of the adsorbent for most effective work.

The best adsorbent carbons can not be made directly from wood charcoals. With the exception of a few hard woods, of which the supply is negligible, the wood chars are too low in density even before activation. Only by pulverizing low density wood charcoals and briquetting them to denser chars can they be made to compare with dense nut chars. On the other hand, coconut shell chars as obtained immediately after distillation are too high in density. Therefore, after the differential oxidation is substantially completed, the oxidation process must be continued through a definite secondary stage, until the critical apparent density is reached, if the maximum adsorptive capacity is to be attained.

In commercial practice the rapidly mounting costs of continued oxidation sometimes make it advisable to stop short of the ideal or theoretical density for certain industrial uses. In other cases high capacity is so vitally important to the efficiency of the process that the higher cost of carbon becomes a secondary matter. This is also true of carbon for military purposes. The engineer must determine in each case to what extent space and high capacity per unit of volume are vital factors, and be prepared to pay the necessary premium for his requirements.

The first quantitative criterion employed in defining and measuring adsorptive capacity was the tube tests developed and used by the Chemical Warfare Service of the United States Army as specifications for gas mask carbon.⁴⁰ Air containing a known concentration of toxic vapor such as chlorpicrin was passed at a constant rate into a tube of fixed diameter containing a 10-centimeter layer of carbon of a definite fineness. The capacity of the carbon was then expressed by the number of minutes to the break point, — that is, to the point where a detectable trace of vapor appeared in the exit air. The weight of gas adsorbed at the break point

⁴⁰ J. Ind. Eng. Chem., vol. 11, p. 519 (1919).

was determined directly. This test of course has many defects, for the break point is affected by the concentrations of the vapor, the rate of flow of the air, the fineness of the carbon, and other factors, all of which bear no relation to the intrinsic character of the carbon itself. The break point corresponds to the point when the rate of adsorption falls below the rate at which the gas was being passed through the tubes. This critical point appears to be reached when the residual unsaturated capacity of the carbon drops to a constant minimum value depending upon the particular factors of the test.

If pure air be passed over the carbon, either after the break point on a tube test or after the carbon has been saturated by coming to equilibrium with a definite concentration of a gas at a definite temperature, the losses of adsorbed gases are first very high and then fall to a gradual and almost negligibly slow rate, too slight to be detectable by the usual methods. The weight of adsorbed gas corresponding to the period of extremely slow removal in a current of air is termed the retentivity of the carbon. The retentivity value for a series of typical carbons seems to bear no fixed relationship to the saturation values, but to show a most significant correspondence to the value of the carbon for vapor recovery from low concentrations, adsorbing power for removal of substances in true solution such as iodine, and the relative value for different kinds of toxic gas removal. A large amount of data has been collected by a number of workers in the field which seems to show that the retentivity values correspond most nearly to the so-called specific adsorptive capacity which is associated with the chemical properties of the active carbon. It is held then that the excess of more easily removable gas or vapor was maintained by capillary forces associated with the physical or microscopic structure of the carbon. The specific adsorptive power is believed to represent specific polar forces or the activity of secondary valences on the surfaces of the carbon atom.

Any method or process of releasing carbon from its compounds at sufficiently low temperatures in the absence of hydrocarbons or other strongly adsorbed substances should yield active carbon directly. The requisite physical structure for the production of commercial gas-adsorbent carbons can be obtained only in suitably prepared chars, cokes or coals termed primary carbon. These all require activation. High temperature calcination has been employed. The stabilization of the hydrocarbons by adsorption, however, usually raises their final decomposition temperature above the critical temperature range for the formation of active carbon, and inactive carbon results from the decomposition of the hydrocarbons. A limited degree of activation can be effected by the use of selected chars having a low decomposition point. The wood charcoals employed by the British and French for gas masks were chiefly prepared by this method. The process does not permit control of the resulting porosity of the carbon granules. It is only effective on chars of low density which give materials of low structural strength and low adsorbing capacity per volume of adsorbent. The German gas mask carbon was prepared by carbonization of materials impregnated with a variety of metallic salts or oxides before carbonization. These mineral salts, particularly zinc chloride and related compounds, were effective in preventing the formation of the adsorption complex of hydrocarbons or in causing their decomposition when they were adsorbed. The metallic oxides formed during carbonization were dissolved out by hydrochloric acid. This provided an exceedingly porous structure with capillary pockets of molecular dimensions. These carbons possess a relatively high capillary capacity but only a limited specific adsorption similar to that of active carbon. Lenher⁵⁰ has proposed to dissolve the hydrocarbons away from the primary carbons by a solvent such as selenium oxychloride.

The method of activation of wide application as well as

⁵⁰ Chem. & Met. Eng., vol. 25, pp. 109-121 (1922).

great flexibility is one depending on the differential oxidation of the non-active carbon. This is carried out by either wet or dry methods, the oxidizing agents usually being gases such as air, steam, carbon dioxide, chlorine or similar materials. The hydrocarbon constituents of the adsorption complex are slightly less resistant to oxidation than is the active carbon. By a proper adjustment of the temperature and concentration of the oxidizing material, the adsorbed hydrocarbons may be effectively removed and the formation of inactive carbon reduced to a minimum. The product obtained by air activation is ordinarily inferior to the best steam activated products because the difficulty of carefully controlling the temperature and rate of an exothermic reaction is much greater than is the control of an endothermic one.

Ostrejko, an Austrian, worked out the essential features of the steam activating process a year or more before its development in America. For military reasons his patents were withheld from issue in Austria until after the war. His disclosures, therefore, were unknown until after the American processes were in operation by the Chemical Warfare Service. Neither Austria nor Germany seemingly developed or employed his methods.

A good gas-adsorbent carbon should have good mechanical strength, optimum density for its particular use and a high activity. Mechanical strength is necessary to avoid packing, crushing and dusting in containers or towers to which large volumes of gas must be passed at high velocities. Military and industrial gas absorbing vessels are rated upon the size of the container rather than on the weight of the adsorbent.

In the manufacture of gas mask carbon for military purposes, extensive experimental work shows that the most satisfactory materials were nut shells or fruit pits, among which the preferred material was coconut shells. At the plant of the Astoria Light, Heat and Power Company at Astoria, New York, where the Chemical Warfare Service

of the United States Army manufactured gas mask charcoal, the raw material was carbonized initially in horizontal retorts formerly used to produce coal gas. After carbonization, the raw material was crushed and screened between 8 and 16 mesh and then submitted to activation which consisted of air or steam treatment. At various times gas mask charcoal has been made from anthracite and a number of other carbonaceous materials, as well as various kinds of woods and nuts.

The retorts were of semi-elliptical cross section, 20 ft. (6. m.) long, 2 ft. (60 cm.) wide, and 18 in. (46 cm.) high, arranged in banks of two rows of four retorts each, one above the other. Four banks constituted a bench. Every retort had a door at each end opening to the full size of the cross section of the retort, which was clamped shut except during charging, drawing or raking the charge. The retorts were heated to about 900° C. by hot gases from coke fires situated at each end of the bank and passing through flues around the retorts. Charging was accomplished by buckets about 10 ft. (3 m.) long on the traveling boom of a charging machine, one at each end of the retorts. The charge was pushed out by a semi-elliptical plate, a little smaller than the cross section of the retort. Temperature readings in retorts and flues were taken every two hours.

The air-treater was a set of 5 iron tubes, set one above the other in a combustion chamber, at a slope of about 3°. Each tube was 12 ft. long, with an inside diameter of 12 in. A 10-in. screw conveyor running the entire length of the tube tangent to the bottom, conveyed the carbon through the tube. Each combustion chamber contained two sets of these tubes, heated by gas burners at the bottom of the chamber to about 400° C.

A method was later developed whereby the carbon from the retorts was treated with steam, producing a much better quality than when the product was air treated. The furnace for this process consisted of a vertical gas-fired combustion chamber 7 ft. (2.1 m.) high and having an inside diameter

of 27 in. (68 cm.). This surrounded a nichrome reaction tube having 3/4 in. (19 mm.) walls and an inside diameter of 7 in. (17.8 cm.). Coal gas mixed with air in premix burners was used as fuel. Inside the nichrome reaction tube was a 2 in. (5 cm.) nichrome pipe extending the entire height of the furnace and perforated all around for 8 in. (20 cm.) at about the level of the center of the combustion chamber, with 1/4 in. holes. This pipe was the steam jet. The best carbon was produced when treated with steam at 950°. To obtain this temperature in the mass of charcoal, it was necessary to maintain a temperature of 1150° in the combustion chamber at a level about 27 in. above the gas burner.

The gas mask in its present form is the highly developed and efficient product of extensive and careful investigation. It is light, quickly applied, allows freedom of movement and is purchasable at a reasonable price. It affords effective protection against such gases and vapors as the materials in the canister are designed to adsorb. Charcoal as an adsorbent is of the most general application. Most canisters are charged with materials intended to adsorb only a limited number of closely related gases. The contaminant in the air must be known and the proper canister employed to adsorb that type of gas. There is one type of canister, the so-called "all service" variety which gives protection against all gases and vapors found in industry, except, of course, high concentrations of the simple asphyxiants. This type of canister is useful when the contaminant in the air is unknown. Its application is quite important in the case when firemen enter chemical storage depots. It has the disadvantage of a relatively short life, owing to the comparatively small supply of each adsorbent in the canister when used against any one particular gas.

RECOVERY OF GASOLINE FROM NATURAL GAS

Gas adsorbent carbons, particularly those of the coconut type, are coming into greater industrial use for the recovery

of gasoline from natural gas, and the recovery of solvent vapors such as those of petroleum ethers, benzene, sulphuric ether, ethyl acetate, alcohol and similar materials from air. Charcoal is also used for the recovery of products of fermentation occurring in the waste gases from fermentation vats, such as acetone, butanol and alcohol; for the purification of gases by the removal of sulphur and related compounds by adsorption, as well as the recovery of benzene and light oils from illuminating gas. It is sometimes employed for the recovery of the oxides of nitrogen, sulphur dioxide and similar materials. There are a number of plants in Continental Europe employing activated carbon for the extraction of benzol and toluol from coal gas. In practically all cases the method of plant operation is the same and the types of plants in their construction are quite similar.

As it is used in the natural gas industry, charcoal is placed in two, three or more adsorbers. These are cylindrical towers or chambers which serve to hold the charcoal. The material is of the 8 to 14 mesh size supported in the adsorbers on screens of such mesh as to hold the charcoal but still allow free passage of the gas. In operation of the plant, one adsorber is always adsorbing, one distilling and one cooling. Natural gas is passed through one bed of charcoal until the latter has adsorbed its quota of gasoline. Charcoal will retain about 10 to 20% of its weight of gasoline before some of the latter begins to escape. Next the gas flow is diverted by means of appropriate valves to another adsorber and saturated steam is forced through the first charcoal bed, driving out the gasoline previously adsorbed. The gasoline vapor and steam are condensed in water-cooled condensers and the water trapped from the gasoline. In order to cool and dry the previously steamed charcoal in preparation for a subsequent adsorption, residual gas is passed through the bed of carbon. The residual gas is the natural gas after it has been stripped of its gasoline content. The adsorbers are thus operating in cycles of adsorbing, gasoline removal and cooling.

Natural gasoline is essentially a mixture of paraffin hydrocarbons, the first of which — methane — is the least readily adsorbed by charcoal. The next member — ethane — is more readily adsorbed than methane, propane more readily than ethane and so on. When natural gas from which the gasoline is to be extracted first comes in contact with the charcoal, part of it is adsorbed. Although the gasoline constituents are more readily adsorbed, there are not enough of them present to satisfy the adsorbing power of the charcoal. As a result, some of the other constituents of the natural gas are also taken up. As the gas advances through the charcoal bed to the outlet, all of the charcoal is saturated in this manner. As the flow of gas continues, more of the gasoline constituents are taken up. As they are adsorbed they displace the lighter and undesirable constituents of the gas until finally all of the gasoline constituents which can be retained are condensed within the pores of the charcoal, until the latter is saturated. The gas is then turned into a fresh adsorber where the process is repeated.

The removal of the gasoline from the charcoal is termed distillation. Live steam is turned into the adsorber in direct contact with the charcoal. Steam at 215° F. simply heats the charcoal until most of the gasoline is removed, but a steam temperature of at least 575° F. is required for the complete removal of the gasoline. At the end of the distillation period, the charcoal will retain some gasoline and water vapor. It is cooled with residual gas from a fresh adsorber. The retentivity of the charcoal will cut down its adsorption capacity for gasoline in all subsequent adsorptions after its first time use.

Figure 38 gives a diagrammatic plan and layout for a commercial gasoline extraction process, using charcoal as an adsorbent.

ABATEMENT OF INDUSTRIAL STENCHES

There are many industrial processes which give off objectionable odors and vapors. The particularly obnoxious

odors given off during the rendering of slaughter-house waste and other waste fats to recover tallow are quite familiar. The use of activated carbon as an adsorbing ma-

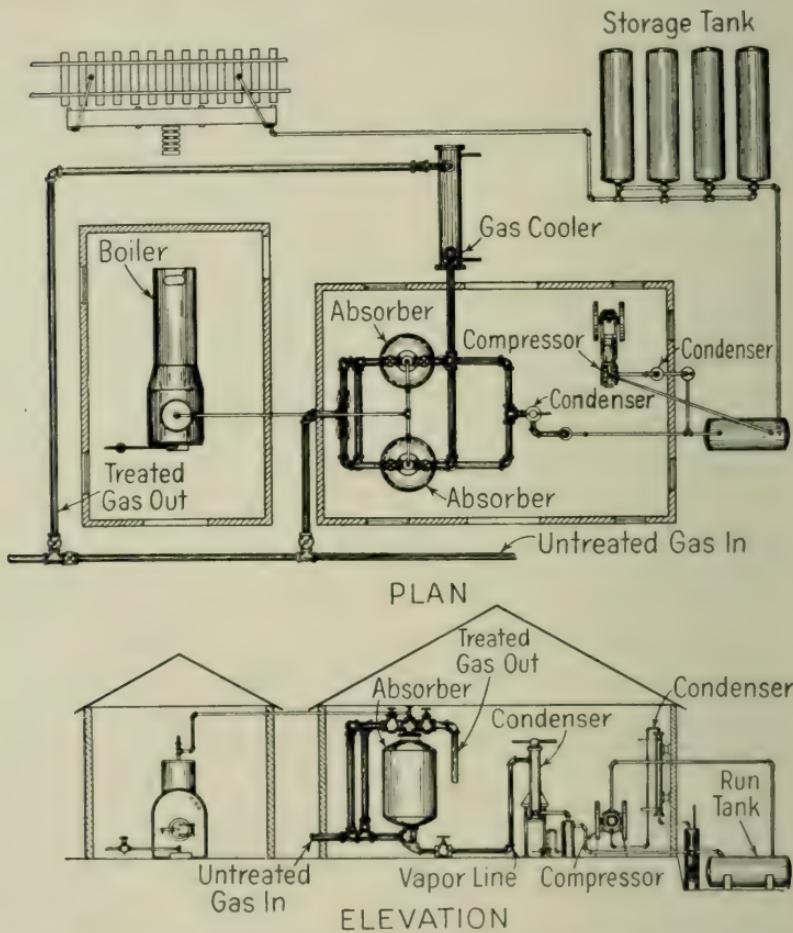


FIG. 38.—PLAN AND ELEVATION OF GASOLINE EXTRACTION PLANT
USING CHARCOAL ABSORPTION PROCESSES
(Note: third absorber not shown)

terial has been developed particularly for employment in connection with large city garbage and waste disposal plants.

Gases or air containing the odoriferous materials or stenches are conveyed to adsorbers of the same type and

variety used in gasoline recovery. The activation of the used carbon by steam is the same with the exception that the condensate is trapped off to a sewer. Any uncondensed vapors and fixed gases distilled out of the carbon by the steam are burned either in the fire box of the boiler or otherwise to insure complete combustion. The revivified carbon is cooled after steaming by passing cold air through it or by water in pipes in the carbon.

A diagrammatic layout of a stench-abating installation using activated carbon is shown in Fig. 39.

The length of time which the carbon may be in service before it becomes saturated with the foul products and must be revivified will, of course, depend upon the amount of foul materials passed through it per unit of time. Since the actual weight of foul materials in the air is usually very small, the carbon will remain effective for a considerable time interval. In some cases it has been the practice to revivify the carbon once a week. This period may be longer or shorter, depending upon the service required. The passage of 150 cu. ft. of air per minute to a cylindrical bed of 8 to 14 mesh carbon 5 ft. deep and 3 ft. in diameter will require a pressure of about $\frac{1}{2}$ lb. This is sufficient to maintain a positive suction on vats, kettles or in ventilating systems so that odors may be removed from their source of generation.

The deodorization of industrial gases, particularly carbon dioxide, from fermentation tanks so that the material may be employed in beverages is a modification essentially of the plant used for stench abatement. Adsorption is in cycles, the adsorbed material being removed from the carbon by steaming and the drying of the carbon ordinarily done by means of closed steam coils around which the carbon is packed. A plant to deodorize completely 200,000 kilos of carbon dioxide per month from fermentation vats consists only of a pair of adsorbers $2\frac{1}{2}$ ft. in diameter by 5 ft. high, with necessary condenser, heating and cooling coils and auxiliary piping. The floor space in comparison to the work done by the plant is exceedingly small.

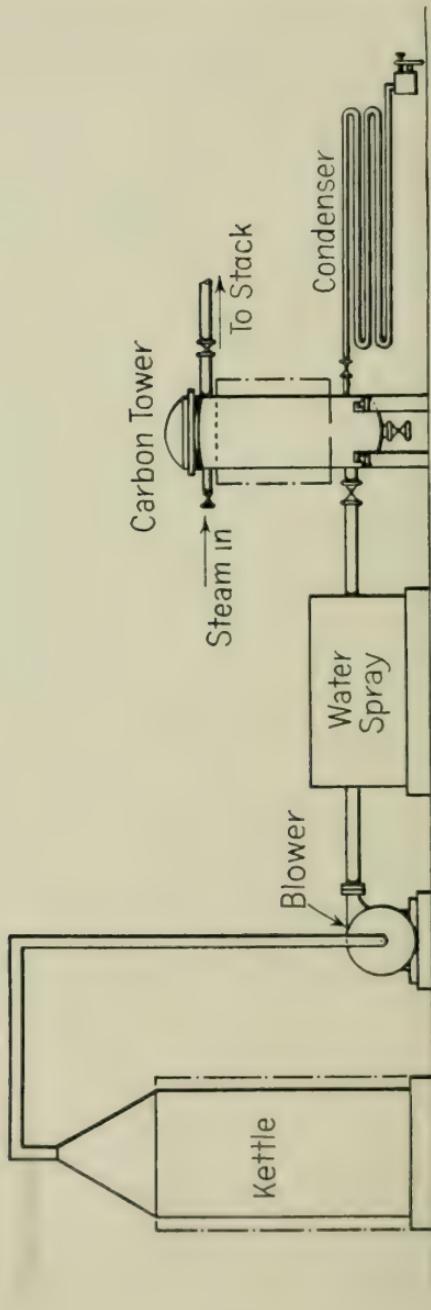


FIG. 39.—DIAGRAMMATIC LAYOUT OF STENCH ABATING INSTALLATION USING ACTIVATED CARBON

The employment of activated carbon has been suggested for the purification of hydrogen and nickel carbonyl for hydrogenation purposes, and the purification of ammonia before its catalytic oxidation to nitric acid.

The field for activated carbon as a gas adsorbent is very large, and at the present time very little explored. An interesting application of activated carbon has been the adsorption of sulphur dioxide from industries, particularly of metallurgical type, to prevent the destruction of outlying farm and forest lands by the sulphur dioxide in the waste gases. The adsorbed sulphur dioxide may be recovered from the charcoal and used for sulphuric acid manufacture.

While in America the activated carbon of the gas-adsorbent type most widely used is that made from coconut shells and fruit pits, on the Continent gas-adsorbent carbons made from raw materials such as sawdust, peat, etc., are extensively employed. One of the most prominent of these is that of Urbain which is made from peat, employing phosphoric acid as the activating material. Peat of good quality, containing as little ash as possible, is dried, ground, mixed to a paste with phosphoric acid and then extruded through the die of a hydraulic press. The die may have one or more openings, the material extruding as threads. The threads which come out of the press are broken by simple agitation in a rotating vat. After a time the fragments harden as a result of the slow reaction between the phosphoric acid and the vegetable material. Carbonization takes place to some extent during drying, which is done by means of hot air or waste furnace gases. Drying is followed by calcination in gas retorts open at one end where the phosphorus is recovered as phosphoric acid. After an 8 to 10 hour calcination period at a final temperature of 1,000°, the carbon is washed with hydrochloric acid to remove mineral matter, then dried at about 300° and placed on the market. After manufacture, the carbon is in the form of short cylinders, 5 to 10 mm. long, with rounded ends, and 2 to 3 mm. in diameter. In comparison to coconut char on a volume to vol-

ume basis, the material has a lower capacity as expressed in weight of adsorbed constituents. On a weight to weight basis, it is stated to be approximately the equal of the best coconut chars. As has been stated before, a number of commercial carbons made from a large variety of raw materials on a weight for weight basis are good gas adsorbents when compared to coconut char, but on a volume to volume basis are less efficient.

German gas works are taking up the Bayer method (D.R.P. 310,092, Nov. 4, 1916) developed by F. Runkel, of adsorbing benzene from gas by means of wood charcoal.⁵¹ The adsorption is very nearly complete, until 1 kg. of charcoal has adsorbed 400 g. of light oils. It also adsorbs carbon bisulphide, naphthalene and tarry substances, the latter being washed out of the pores with wash oil. A succession of carbon filters fractionate the condensates to a large extent. The method has been in use for some time in cellite, celluloid, and powder factories for recovery of ether, alcohol, acetone and benzene. Benzene yields may be increased 10 to 20% by this method.

Hoffert has made several experiments for the recovery of benzene by activated carbon.⁵² He determined the relative adsorptive capacities of the active carbons and a silica gel by saturating at 20° with a benzene air mixture containing 0.86% by volume of benzene. Urbain carbon showed 36% by weight adsorption, coconut 32%, Bayer T carbon 28%, and silica gel 18%. The adsorptive efficiency of each was 98%. Carbon showed a preferential adsorption for benzene unaffected by water vapor up to the break point. Silica gel removes water vapor quantitatively and shows a fairly high capacity for benzene. Adsorptions by weight of adsorbent were: carbon 15 to 30%, silica gel 8 to 14%; or carbon, 5.8 to 11.6 g. per 100 cc. adsorbent space, silica gel 5.7 to 10.0 g.

⁵¹ Gas und Wasserfach, vol. 64, pp. 205-6 (1921); J. usines à gaz, vol. 45, pp. 170-1 (1921).

⁵² Gas J., vol. 170, pp. 654-5 (1925).

CHAPTER XVII

BONE BLACK

BONE BLACK or bone char is the carbonaceous residue obtained as a result of destructive distillation of bones in the absence of air. Only fresh, hard bones free from extraneous matters can be used. Whale, fish bones, and the skeletons of marine animals are unsuitable as they produce a soft char. Bones exposed to atmospheric action or buried in the ground, due to their decomposition give chars deficient in carbon.

The principal constituent of bones is tricalcium phosphate. Beside this compound, bones contain magnesium phosphate, calcium carbonate, some alkaline salts, and fatty and cartilaginous matter intimately associated with the mineral contents.

Bone cartilage consists essentially of carbon, oxygen, nitrogen, hydrogen and sulphur, containing these elements in approximately the proportions shown in the table below:

	<i>Per cent</i>
Carbon	50
Oxygen	25
Nitrogen	17.5
Hydrogen	7.0
Sulphur	0.2

Bones of young cattle contain more cartilage and less mineral matter than bones of older cattle. The latter, however, are generally richer in fatty material.

In the manufacture of bone char, the bones as received are first sorted. They are then crushed, usually in a gyratory, and cut up in a cutting machine. The product after

this operation consists of small splinters a few inches in length.

Fat and oily matter are removed either by boiling or rendering or by solvent extraction. The usual solvent extractants are naphtha and benzine aided by live steam. The benzine is recovered by gravity separation, as its density is less than that of the condensed water. The fat is later purified by boiling with water and steam to remove any traces of the solvent it may have retained. If the extraction is properly conducted, the bone cartilage is little affected.

The bones thus treated are placed in retorts which are carefully closed to keep out the air. The retorts are then brought to a red heat, which temperature is necessary to effect the desired destructive distillation of the bones. Vertical or horizontal iron retorts are used, commonly operated in banks of five or seven. The carbonizing plant is quite similar in appearance to a gas works, and many forms of gas retorts have at one time or another been adapted to bone char manufacture. The offtakes of the retorts are connected to a hydraulic main, then to condensers, then to scrubbers filled with coke in which the bone oil separates out, and finally to ammonia scrubbers. The cleaned and stripped gas is used for heating and lighting. All of the operations are similar to those of by-product coke plants. Charges of 2½ cwt. in the vertical, and 500 cwt. in the horizontal retorts are used. Carbonization takes 6 to 8 hours in the former case, and 8 to 10 in the latter. The bone oil produced is 3 to 5% of the weight of the original bones. The ammonia on the basis of ammonium sulphate is about 8%, although some Continental works report that they obtain 14% of ammonia on the basis of ammoniacal liquor. The gases amount to approximately 20% of the weight of the bones and the tar 6%. The bone char in its final cooled form usually shows a yield of 60%. When the carbonization is complete, the bones are removed from the retort and cooled in sheet iron air tight canisters. When cold, the char is crushed in a mill and screened into the various grades and

sizes required by the consuming trade. Good bones give 60 to 65% of char but 20 to 30% of this is low-priced dust. One ton of new char will occupy 48 to 54 cu. ft.

While the mineral constituents of the bones suffer only slight or no chemical changes in the process of distillation, the organic compounds present undergo great changes and modifications.

The carbon remains in part as fixed carbon in intimate association with the calcium phosphate. A part of the carbon passes over with the non-condensable gases in the form of hydrocarbons. Some of it combines with oxygen as carbon monoxide or dioxide, and a small part of it enters into combination with nitrogen as cyanogen or passes into the form of cyanides or other complicated amino or nitrogenous compounds.

The tar and oil account for a very high percentage of the nitrogen. The nitrogen of the bones is also found as ammonia, appearing chiefly as ammonium carbonate, or, if sulphuric acid be used in the adsorber, as ammonium sulphate. Ammonium sulphide and hydroxide are also formed.

The char always retains a certain percentage of nitrogen. A good quality bone char should have not less than 9% nor more than 11% of carbon, a maximum silica content of $\frac{1}{2}\%$, maximum ferric oxide .15%, a maximum calcium sulphate of .2%, a maximum water of 8%, with a minimum weight of 52 lbs. per cu. ft. The char will contain from 70 to 75% of tricalcium phosphate and perhaps a small amount, usually less than .1%, of calcium sulphide. The material should be dull black in color. The ash resulting from ignition should be uniformly white or cream tinted. A new, well burned char will have a firm physical structure and high degree of porosity and a somewhat metallic ring when struck.

Uniformity of grain is of considerable importance and great care is taken to grist the char properly. The fine dust which unavoidably results is turned into fertilizer or is ground up for the manufacture of ivory black.

New char varies materially in its composition according

to the quality of the bones used and to the method of manufacture. Below are given analyses of new char from various countries, the first column representing an English bone char, the second an Austrian, and the third an American.

	(1)	(2)	(3)
Carbon	10.76	9.28	9.30
Sand, etc	0.29	0.32	0.42
Tri-calcium phosphate	73.50	75.10	75.00
Calcium carbonate	8.69	7.40	6.23
Calcium sulphate	0.05	0.10	0.08
Calcium sulphide	0.03		0.01
Calcium oxide		0.91	
Magnesium phosphate	6.08		
Ferric oxide	0.16	0.34	0.23
Alkaline salts	0.44		

In use, the carbon, the calcium phosphate, the iron oxide and the calcium sulphate generally tend to increase; the calcium sulphide should be kept down as low as possible by proper regeneration; the calcium carbonate decreases.

A char which had been in use for a considerable time, and which may be considered as a fairly typical example, was found to have the following composition:

Carbon	11.50
Sand, etc.	0.75
Tri-calcium phosphate	82.00
Calcium carbonate	2.70
Calcium sulphate	0.65
Calcium sulphide	0.11
Ferric oxide	0.47

THE HISTORY OF BONE CHAR

As early as 1792, Lowitz recognized the deodorizing and decolorizing effect of carbonized plant tissues. A little later, Guillon suggested the use of wood charcoal for decolorizing sugar solutions. Kehls in 1793 found that carbon obtained from animal tissue also possessed the property of removing

colors from solution. The work of Figuier in 1811 showed that carbon of animal origin was much superior to the vegetable carbons produced at that time.

Bussy, Payen and Desfosses in 1822 in their prize essays on the decolorizing action of carbon, concluded that the decolorizing properties depended entirely on the physical structure of the carbon, especially on its porosity and its fine state of division.

Stenhaus¹ in 1857 discussed the fact that a carbon like bone char which contains a great amount of mineral matter which prevents sintering or the fusing together of the particles, possesses a very great decolorizing power. This idea was the basis for the production of numerous synthetic chars that were patented about that time and even later, consisting of mixtures of phosphate rock, sawdust, glue, etc. On the other hand, a char which has been exposed to a very high heat and which has thereby been more or less converted into graphite, loses this property of decolorizing to a very great extent.

By agreement the credit for the introduction of animal charcoal into the sugar industry is usually given to Derosne, who started its use in 1812. In the earliest days, bone black was added to the sugar solution in the form of a fine powder. It was boiled in with the syrup and the mixture was then filtered through linen bags. The black was discarded after its initial use. Acid washed bone black was also used in this way, as well as blood char, and partially charred animal matter. The stuff was so rancid as to cause prejudice against its use.

The suggestion that bone char could be regenerated and used over again was made by Dumont and Schatten. The former in 1828 suggested the possible advantages from the use of the char in a granular instead of a powdered form.

About 1855, two commercial forms of bone char were used in the industries. The first was the regular form of the product made in the usual manner. The second was a

¹ Ann. der Chemie. und Farmacie, vol. 101, pp. 244-245.

modification known as purified animal black, prepared by digesting the ordinary product with hydrochloric acid and water until all the lime salts had been removed. It sold in England at two shillings per pound. This material, provided it had been dried in not over 100° C., was very porous and of a dull black lustre. In neutral and acid solutions it was an excellent decolorizer. It lost much of its porosity and decolorizing power if heated much above the boiling point of water.

THE ACTION OF BONE CHAR

The manner in which bone char performs its work has been for many years a very mooted question.

Early in its industrial history, Wallace ² in 1865 suggested that the active body which effected decolorizing by bone char is a compound of carbon and nitrogen. Patterson ³ isolated a nitrogenous substance from bone char which, according to his data, was even more active as a decolorizer than the char from which it was obtained. He stated, therefore, that the active principle of the char was comprised of the nitrogenous bodies present. The work of Horton ⁴ and his colleagues at the Audubon Sugar School of the University of Louisiana, has definitely shown that bone char owes its power of removing color to the presence of active carbon, and that the nitrogenous material serves as a reserve to supply fresh carbon upon re-ignition. In general, he assumes that the activity of a char from any source is due to the same form of amorphous carbon produced by the low temperature decomposition of vegetable or animal substances. Usually the carbon surface is coated over by a layer of ash or hydrocarbons. The char may be activated by the removal of this film. In the case of bone char, the surface film is definitely soluble in water or dilute acids. Patterson's theory has been com-

² Proc. Glasgow Phil. Soc., vol. 6, 1865, p. 377.

³ J. Soc. Chem. Ind., vol. 22, 1903, p. 608.

⁴ J. Ind. Eng. Chem., vol. 15, 1923, p. 519. Chem. and Met. Eng., vol. 32, numbers 1, 2, 3.

pletely overthrown and the action of bone char has been satisfactorily explained according to our physical and chemical laws.

Another theory of the action of bone char states that the greater part of the color absorption appears to be mechanical through the entanglement of the large molecules of colloidal coloring matter in the fine cellular structure of the carbon. A few minutes' consideration will show that this explanation is decidedly lacking in many respects. If color be removed by mechanical entanglement, bone char should be almost as good after all the carbon has been burned off. The structure cannot then be essentially different. But bone char with very low carbon content is a very poor decolorizer. The mechanical entanglement theory does not explain how bone char removes caramel which is not ordinarily considered to be colloidal. Aluminum hydroxide will not remove caramel color from sugar solutions but bone char will. The mechanical entanglement theory does not explain the selective absorption of bone char. As a theory, it has too many shortcomings to be tenable.

Another chemical theory held that carbon dioxide, condensed in the pores of the char, removed lime from sugar solutions by precipitating the same as calcium carbonate, and that the decolorizing of sugar solutions was effected by oxygen condensed in the char. No attempt was made to explain the mechanism of the condensed carbon dioxide and the lime or calcium salts. It is not possible to pump oxygen out of a char or to obtain it by subjecting the char to very low pressure and heat. The assumption of condensed oxygen in the pores of the char is not justified. Some others proposed the idea that hydrogen peroxide was the source of the active oxygen assumed to be the decolorizing agent. It is interesting to note that hydrogen peroxide solutions are decomposed by bone char. The condensed gases theory is decidedly insufficient.

Von Lippmann⁵ refers to the fact that when a concen-

⁵ Die Chemie der Zucker Fabrikation, Braunschweig, 1904, p. 1230.

trated sugar solution at 85 to 95° C. is poured on fine grain bone char, so violent a reaction occurs that caramelization results. Large quantities of water vapor may be formed and minor explosions occur. If the char has been previously wetted, this will not occur. The caramelization may be due to the heat of wetting of bone char, which has a positive value. Caramelization is an exothermic reaction. It is stated to be auto-catalytic. In concentrated liquors it needs only a start.

In the light of all the recent studies made, it seems likely that chemical reactions play only a secondary rôle in the remarkable property of decolorization and purification exercised by bone char. Certainly the great value of bone char industrially is dependent upon its enormous surface and its absorptive properties.

Properly made bone char preserves the cellular structure of the bones from which it was made. According to Horne,⁶ the most desirable size is 16 to 20 mesh, as this wears down more slowly. Appreciable amounts of materials of smaller size than this retard filtration. The size of the grain of the char, the degree of temperature at which filtration is conducted, and the degree of concentration of the filtered solution are all factors of importance in determining the efficiency of the char. Bone char is generally bought on contracts which call for delivery of certain sized materials. Too much fine or too much coarse may cause the shipment to be rejected.

Examined under a suitable magnifying power, each grain of char will be seen to consist of a series of cavities connected by a very great number of minute tubes and channels. The framework of this cellular structure consists essentially of the phosphates and carbonates of calcium. The framework is entirely coated or lined by a deposit of carbon in a state of very fine subdivision. The actual surface of bone char is enormous.

Bone char has great absorptive qualities. It exercises a

⁶ J. Ind. Eng. Chem., vol. 12, 1920, pp. 1015-1017.

selective absorption for different substances, that is to say, when it has become completely saturated with respect to certain coloring matters or to certain salts, it can yet continue to take up and hold other coloring matter and other salts in absorption.

There is no doubt that the refining power of bone char resides in its activated carbon content. If char granules are burned in the presence of air, the carbon passes off as carbon dioxide, leaving the phosphate structure. This phosphate skeleton possesses little or no decolorizing action, although its power of removing dissolved salts remains. Similarly, if the carbon be separated from the other constituents by acid treatment, it retains its decolorizing power, although to a reduced extent because it is not spread out to the great area it occupied on the phosphate skeleton of the char.

The condition of the carbon surface and the area over which it has been distributed are most important factors. It has often been suggested that the carbon in a new char should not exceed about 10% and refiners have been known to refuse char of a higher carbon content. They were probably guided by the fact that the refining power of a char decreased as the carbon content increased. This in no way determines the amount of natural carbon which ought to be present in a new char. Provided the carbon is in an active form, its surface is in suitable condition, and it is properly distributed over the phosphate skeleton, the maximum amount of carbon permissible in a bone char might quite advantageously be greater than that naturally occurring.

Decrease in its porosity is due to an obstruction of its channels and pores by the accumulation of incompletely burned carbonaceous material, by a sintering of its structure under the influence of high temperatures, or by a glazing due to the fusing of silicates absorbed from the solutions.

United with the carbon of bone char there is some hydrogen and some nitrogen. These elements are so intimately associated with the carbon that even very high temperatures will not cause their dissociation and removal.

In new char possibly one-tenth of the so-called carbon is nitrogenous organic matter. Continued use and regeneration gradually lowers this until old char may retain but 2 per cent, or even less, of nitrogen compounds.

The original source of this nitrogen is, of course, the cartilage which occurs in the bones, and which, it will be recalled, contains as high as 17 to 18 per cent of this element.

In what form this nitrogen is present is still open to question. Stolle⁷ held it to be present in the form of cyanogen compounds and believed that the loss in weight, which the so-called "carbon" experiences on burning the bone char, is due mainly to the destruction of cyanides. He supposed the cyanides to be the principal agents in effecting decolorization.

New bone char always contains ammonia and ammonia salts, which should be removed, as far as possible, before use; ammonium carbonate is always formed by the process of destructive distillation and later, in the kiln burning, during revivification.

Weichman⁸ states that "The best way to remove this substance is by a most thorough washing and by the passing of live high-pressure steam through the char while in the filters. In this way most of the gases in the pores of the char are driven out and water is left in the pores, a condition which predisposes favorably to the filtration of liquors."

THE USE OF BONE CHAR

The ideal char granule should have a porous structure which will not shrink during burning, become worn by constant handling, or be adversely affected by acids which may be present in the liquors or wash waters. At the same time, the material of the structure ought to possess the power of abstracting dissolved salts present in the raw sugar liquors. A highly active carbon should be distributed throughout the

⁷ Zeit. D. Ver. Deut. Zucker. Ind.: 1900 and 1901.

⁸ Sugar, p. 436, Nov. 1917.

porous structure, which carbon should possess much greater refining power than that of the carbon which occurs naturally in the char.

The sugar refiner designates chars by their uses in stages of sugar refining as new char, which is new material made from bones; stock char, which is new char after it has been washed and burned several times and is at the start of its life in the char house; wet or used char, which is stock char after it has refined sugar solutions, has been washed in the filter and is ready for revivification; dry char, which is revivified stock char ready for packing into the filter; and spent char, which is stock char which has reached the end of its life in the refinery and has been rejected owing to diminished refining power.

Upon complete combustion, new char yields an ash of white chalky appearance. Spent char gives an ash of glazed appearance and of a reddish tinge.

In its use in sugar refineries, the bone char is contained in large vertical cylinders originally made of cast iron or steel plate. They are generally from 20 to 22 ft. high and from 6 to 14 ft. in diameter, the greater the diameter the less the height. These dimensions will vary, of course, with the size of the refinery, the rate of filtration, the desired time of contact between the sugar solution and the bone char, and the age of the char. The bottom of the filter is conical in shape. Perforated plates covered with a coarse blanket, on top of which is placed a blanket of closer weave, support the bone char in the filter. The cloth fabric retains the bone char fines carried down by the sugar solution. The top of the cylinder is closed by a cover called the filter head. Discharge of the bone char when necessary for revivification is possible through a number of manholes near the bottom of the filter. Clarification of the sugar liquors is by downward percolation. The liquor outlet is connected to a pipe and an upriser tapped off at about $2/3$ of the height of the filter.

The cycle or run of a filter is started when it is filled with

bone char. The filling must be accomplished in an even and uniform manner. This is sometimes done by hand labor, but in the more modern and larger refineries, the char is spread mechanically. The top of the char in the filter assumes a conical shape.

If the char is packed unevenly and not uniformly, washing channels will soon be made by the liquor being filtered. This will cause an inferior filtration, washing difficulties, and mechanical troubles in handling the sugar solution.

After the filter has been loaded, the sugar solution is slowly admitted to the edge of the cone of the char at the top. It gradually works its way down the sides of the char until it reaches the bottom plate, then flowing across this, rises to the top displacing the air in the char. As soon as the liquor appears in the outside delivering pipe, the outlet is closed and the filter filled more rapidly. When the liquor has reached the top, the inflow is stopped. The filter operator determines that all air is expelled by the fact that the sugar liquor is now quiet and no longer "boils" as the result of displacement of air. The filter head is then put in place, the pressure on the liquid increased, and the clarification then becomes continuous.

It is important that the char should not be placed in the filters at a temperature higher than 130° F. This is assured by thermometric control, the thermometer being placed in the stream of the entering bone black.

Ordinary practice calls for a liquor temperature of 160° to 170° F. There is a decided temperature rise when the sugar solutions are first sent through the char.

The rate of speed at which the liquor is run on the filters is quite important. With high grade liquors from very active char, 1,000 gals. per hour may be allowed; but with lower grade products, the maximum rate of flow is limited to 600 to 700 gals. per hour.

The highest grade sugar solutions should always be sent on first and these followed without interruption by grades lower in purity. If one grade of sugar solution be filtered

exclusively, the char apparently becomes saturated with the particular impurities taken out. As an example, a 96° centrifugal raw sugar liquor will at first come out with practically 100% purity, but if too much of this grade of liquor be used, the purity will gradually become lower and lower until the char, instead of removing, actually gives up impurities to the liquor.

The amount by weight of char to be used per unit weight of raw sugar depends upon the capacity of the char, the purity of the raw sugar filtered, and the rate of filtration. The best average ratio has been found to be 1 lb. of char per pound of raw sugar filtered. It is not unusual, however, to have as high a ratio as 1 1/2 of char to 1 of sugar when poor quality sugars are handled, and as low as 3/4 of char to 1 of sugar when high grade centrifugal sugars are worked. Some classes of raw sugars contain coloring matter which is so difficult to remove that considerable char is required. When refining normal beet sugar less char is necessary to remove color than when refining normal cane sugar. Practically complete decolorization is required to give first refined liquor suitable for cube sugars; and with normal cane sugar which has been properly treated by the affination and mechanical filtration process, from 175 to 225% of char, expressed as a percentage of the dissolved solids in the liquor, may be necessary. The percentages of color and ash removed depend upon the amounts and nature of these impurities present in the clear raw sugar liquor. In the normal way, 200% of char removes about 97% of the coloring matter and from 45 to 55% of the mineral salts. When it is necessary to increase the percentage of char in relation to solids in the liquor, this is done by decreasing the amount of liquor which is passed through the filter containing a constant quantity of charcoal. In order to obtain second refined liquor which will yield granulated sugar, 30 to 40% of char is needed. This ordinarily removes 80 to 90% of the color and 25 to 35% of the ash. The total quantity of char utilized for liquors and mother syrups, expressed as a per-

centage of the raw sugar entering the refinery, varies with the quality of the raw sugar and the percentage of white sugar produced. A refinery making a small proportion of brown sugars must pass more mother syrups over the char than a refinery producing a larger proportion of brown sugars. Generally with cane sugar the percentage varies from 70 to 100%.

In those refineries whose products are only granulated sugars and syrups, the so-called continuous filtration system in which each filter acts as an independent unit is preferred. This method requires a smaller number of filters for its operation.

The soft sugar houses usually favor the so-called set system of filtration in which all filters do the same kind of work at the same time. This method is more advantageous where the liquors are given more than one filtration.

When the char has become so charged with impurities that it will no longer decolorize efficiently, the inflow of liquors is stopped, the level of the solution in the filter drops or it is forced by air pressure to the level of the char. The filter head is taken off, the char cone is leveled and water at very near the boiling temperature is used to fill the filters. The filter head is then replaced and a steady stream of hot water at a rate of 300 to 350 gals. per hour is fed into the filter.

If the filter in the first place has been well charged with the char, and the wash water has been properly introduced, there will not be a mingling of water and liquor, but the latter will be displaced evenly by the water so that for some hours after the washing of the char has begun, the sugar liquors will continue to flow down the filter with their original density.

Gradually, however, the sugar solution becomes less dense. When it has fallen to a prescribed density of, say from about 15 to 20° Baumé (26.7 to 35.7° Brix) it is no longer sent to the liquor or syrup tank to which it had, up to this point, been delivered, but it is now classed as sweet-

water and diverted to the evaporators to be concentrated preparatory to recovery of the sugar content.

Some sugar always remains in the char, no matter how thoroughly the washing may have been done. The cost of water sets an economic limit to the completeness of washing.

The desire to eliminate the expensive char station in sugar refineries has led to considerable experimentation with a view to the substitution of more efficient decolorizing chars and filtration with presses. These will be discussed in other sections of this volume.

A large part of the value of bone char in sugar refining lies in the fact that it not only decolorizes but also adsorbs mineral salts to a great degree.

Horton and Sengson⁹ found that, volume for volume, bone char is much more efficient than Norit in removing mineral matter from sugar solutions. Norit is a very active vegetable char prepared synthetically from birch wood. Weight for weight, there is very little difference in the ash absorption provided the sugar solution is 15° Brix or over. When it is remembered that bone char is used to the extent of about 100% of total solids, whereas Norit and the synthetic decolorizing chars are used to the extent of 5% of the total solids in solution, the supposedly greater ash-absorbing power of bone char is explained.

As has been stated before, after being in use for some time the bone char loses its efficiency and is removed for revivification which is usually accomplished by roasting at a red heat. On much heating its density increases, so that after many heatings a ton of char may occupy only 28 cu. ft. as compared to 54 cu. ft. in its original form. Char can be revivified up to 200 times, which figure represents a life of about two years. After it is not possible to revivify the char to a practical extent for reuse, the spent char is used as a paint pigment and a fertilizer. Its fertilizer value is dependent upon its potassium salt and phosphate content. It is also worked up into miscellaneous blacks such as sugar

⁹ J. Ind. Eng. Chem., vol. 16, pp. 165-167.

house black, the poorer grades of drop black, and as bone black pigments. Very little sugar house black is made at present.

The bone char production of the United States is of the order of 50 to 60 million pounds annually, having a value depending upon the market of $2\frac{1}{2}$ to 3 million dollars.

Senderens¹⁰ found that after bone char was washed with hot hydrochloric acid and distilled water, dried at 100° , it had increased catalytic activity over wood charcoal in the decomposition of ethyl alcohol and propyl alcohol. When ethyl alcohol vapors at 350° C. passed over bone char, Senderens produced

.5	part carbon dioxide
35.5	parts ethylene
4.5	parts of carbon monoxide
54.7	parts of methane
4.8	parts of hydrogen

Under the same conditions propyl alcohol broke down into

87.8%	propylene
1.3%	carbon monoxide
9.5%	ethane
1.4%	hydrogen

He explains the increased catalytic activity as due to silica.

Clark,¹¹ in his study of the action of animal charcoal and sugar, found that at the beginning the ash and reducing sugars are first absorbed and after a while are given up. He states that of two sugar solutions of the same color, the one having the greater salt and reducing sugar content is decolorized less by the char. Ditmar¹² found that bone char from fish was very suitable as a microbe adsorbent. Divenella¹³ found that digestion is materially accelerated by

¹⁰ Comptes Rendus, vol. 144, pp. 381-83.

¹¹ J. S. C. I. vol. 32, pp. 262-265.

¹² Die Umschau, vol. 48, 1914.

¹³ J. Amer. Med. Assoc., vol. 64, 1883.

small quantities of charcoal. It is interesting to note a present day use of Darco, a synthetic char made by carbonizing lignite, as a constituent of digestive tablets.

Kraus and Barbara¹⁴ found that when diphtheria toxin diluted 1 to 10 was shaken with animal charcoal and allowed to stand for one hour, it was without pathogenic activity when injected subcutaneously into a 250 gram guinea-pig. The animal survived without even showing a local edema. A control succumbed to 1% of the dose in 48 hours. They obtained similar results with tetanus and dysentery toxin.

REVIVIFICATION OF BONE CHAR

Originally bone char was used in the form of a powder and discarded after having been used but once. Very soon, however, the advantages of employing the char in granular form were recognized and the methods of reclaiming for repeated use were worked out. In its present industrial applications, its care and revivification are matters of prime importance.

Various processes of revivification differ largely according to the manner which is used in the sugar refinery and the treatment given to the bone char after use but before furnacing.

When a preliminary defecation and filtration through filter bags or presses is the practice, the bone char serves only to remove the coloring matters and some dissolved salts in the sugar solution. In this case, the process of regeneration resolves itself into thoroughly washing the char, completely drying it and kiln burning it.

Revivifying kilns are ovens provided with double or triple runs of pipe through which the bone char passes by gravity. These pipes are generally oval in section, 10 to 14 ft. long and about 3 by 12 inches in diameter.

Regulation of temperature of burning of the char is very important. At too low a temperature the impurities are

¹⁴ Deut. Med. Woch. Schr., vol. 41, pp. 393-394.

insufficiently carbonized; if the temperature be too high, considerable of the carbon is burned. The optimum temperature maintains the retorts at a dull cherry red heat, which corresponds to a temperature of about 750° F.

After treatment in the kilns, the char must be cooled out of contact with the air. It is then screened to remove the fine dust unavoidably formed by the mechanical handling it has suffered.

Where preliminary defecation and filtration is not practised, or where sugar solutions rich in lime salts are sent over the char, the process of revivification is not so simple. An acid treatment is employed ordinarily.

The first step consists of a treatment with hydrochloric acid to remove the lime which is present in the char as carbonate, sulphate, hydrate and as organic acid salt combinations. Only very dilute hydrochloric acid may be used. The acid must be free from sulphuric acid, sulphates and arsenic, so that only the adsorbed lime is removed and the original calcium carbonate and sulphate skeleton of the char is not destroyed. The calcium chloride formed by the action of the acid is readily removed by washing with water.

The next step consists of exposing the washed warm mass freely to the air and its microorganisms. Fermentation soon starts and the organic substances which have been absorbed by the char are broken down. Adsorbed sugar first undergoes an alcohol fermentation, followed later by an acetic acid, then a butyric acid fermentation. After a few days fermentation is stopped by removing the putrescent water. The char is then thoroughly washed.

The fermentation process is so disagreeable that in many instances it is displaced by boiling with caustic soda. The calcium sulphate is changed into sodium sulphate and calcium hydrate. At the same time considerable organic matter is caused to pass into solution.

If, however, the fermentation process has been followed, the next step consists in the removal of calcium sulphate by boiling with the solution of caustic or soda ash. The calcium

sulphate is thus changed into the more soluble sodium sulphate, which may be washed out.

If soda ash is used, the resulting calcium carbonate is removed by treatment with very dilute hydrochloric acid. The use of the alkaline solutions also aids in the removal of the organic impurities which may have escaped destruction in the fermentation process. This is very important as increase in carbon content in the char is avoided and less air is required in the revivifying kiln.

The next and final operation consists in drying the char and kiln burning it. It is most important that the char be thoroughly dried before being heated as there is considerable danger of reducing the calcium sulphate by the carbon and forming calcium sulphide. Hydrogen sulphide gas would be liberated when the material was wet in use, as the alkaline earth sulphides readily decompose. Its corrosive effect on metals is well known. The metallic sulphides which may result will tend to discolor the sugars.

Another method of reconditioning bone char is given in the Scott process in which 1 to 3% of lime, or in some cases 6 to 10% of lime, on the weight of the char, is added after the char has been well dried and the mixture then calcined. The inventor claims the elimination of a large part of the ash, iron and lime salts. Scott claims a saving of approximately $2/3$ of the water needed to wash the char.

A large number of different processes, kilns, furnaces and methods of operating them have been proposed from time to time. The Continental and American patent offices contain a large number of patents dealing with details of revivifying furnaces. The most successful revivifying furnaces call for accurate temperature control with selective oxidation of the organic impurities of the black with measured quantities of air at low temperatures. In this manner the char is not consumed during the time of regeneration; the mass retains its original porosity; calcium sulphide is converted to sulphate; the iron compounds are made insoluble and removal of soluble salts by washing is speeded up.

In the most modern revivifying furnaces, the charging temperature, the moisture content of the bone char, and the

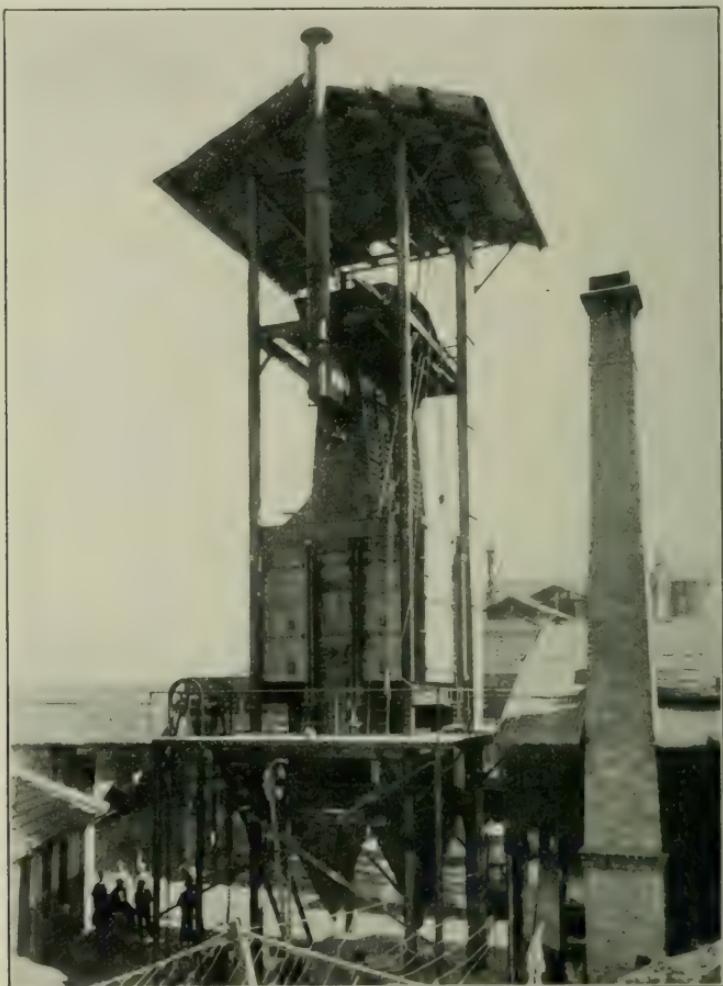


FIG. 40.—A COMPLETE REVIVIFYING APPARATUS
(Courtesy Joubert & Goslin Machine & Foundry Co.)

air supply of the kiln are carefully regulated by special devices. The types of furnaces differ markedly in various parts of the world, some being very simple and some mechanically quite complicated.

Some of the larger bone char revivifiers are huge, with provision for mechanical feeding of the char, drying, burning and cooling, with continuous or intermittent discharge performed either manually or by mechanical means. Fig. 40 shows a completely set up revivifying apparatus. The cooling pipes and discharge hoppers may be seen below the bricked-in furnace. The retorts are vertical or vertically inclined pipes, of large diameter, with relatively heavy walls. Furnace gases and products of combustion heat the tubes which transmit the heat to the bone char undergoing treatment. This heating is thus done indirectly. Furnace stacks, outlets and vents are provided (in some cases in filling, hopper serves as the vent) for the gaseous products resulting from the revivifying process. Air supply dampers are sometimes quite complicated. At times they are omitted in small furnaces, reliance being placed on the amount of air carried in by the char during charging as being sufficient.

CHAPTER XVIII

VEGETABLE DECOLORIZING CARBON

CHARCOAL made by burning wood in a closed vessel has a small power of removing coloring matter from solutions. This property was known as early as the 15th century. The use of wood charcoal as a decolorizing agent seems to have been forgotten until it was rediscovered in 1785 by Lowitz who used it in the production of tartaric acid crystals. Lippmann states that in 1794 an English refinery used wood charcoal in the clarification of raw sugar. Guillou is said to have used wood charcoal in sugar manufacture in 1805. Since that time many processes for the manufacture of decolorizing carbons have been patented. Almost any vegetable substance can be converted into a decolorizing char. The patent literature mentions pine, birch, logwood, quebracho, hemlock, cedar and other woods particularly in waste forms, such as small pieces, shavings and sawdust, corn husks, cobs, corn stalks, cane trash, bagasse, peat, coals of various kinds, lignite, rice hulls, molasses, alcohol slop, waste liquors and extracts resulting from paper manufacture, ivory nut shavings, coconut hulls, peach nut shells and various fruit kernels, olive oil and other vegetable oil residues and pits, and so ad infinitum. All of these yield soft chars. There is consequently loss in handling due to crushing and shattering. The production of a mechanically strong char is one of the problems of the present day. When bone char came into use in the sugar industry at the beginning of the 19th century, vegetable carbons and charcoal were forgotten because of their relatively slight decolorizing power when compared to bone char. Early in the 20th century, however, a number of decolorizing chars made from vegetable matter were introduced and subjected to activating processes which

gave them greatly increased decolorizing power. It is often stated that the future will bring forth the replacement of bone char in the sugar industry by synthetic vegetable carbons.

The vegetable chars are made by the action of heat and chemical reagents on vegetable substances. If vegetable materials be carbonized in closed vessels, the resulting carbon is inactive, — that is to say, it does not possess marked decolorizing power. Any examination of the voluminous literature upon decolorization of sugar and other solutions by carbon suffices to indicate a considerable degree of confusion and incoherence in the technology of decolorizing chars. Theoretical discussions of the inherent properties and behavior of such carbons have notably failed to produce any broad generalization which could adequately satisfy the known facts. Chaney, Ray and St. John¹ state that in their opinion various phenomena relating to decolorizing and adsorptive efficiencies can be correlated and the behavior of any decolorizing carbon fairly accurately predicted on the basis of the generalization that the adsorptive power of any carbon for substances in liquids is directly proportional to its activity, provided the units of the substances to be adsorbed are small enough or the porosity or subdivision of the carbon is great enough to permit unobstructed access to the carbon. They define the activity of the carbon by its retentive capacity for gases, as discussed under gas adsorbents. They further generalize that the adsorptive power of carbon for particles bearing an electric charge is diminished if the carbon bears a charge of like sign and increased if the carbon is oppositely charged. As support for his generalizations, Chaney and his co-workers have plotted the relation between the retentivity of an active carbon as expressed when carbon tetrachloride vapor is used, and its activity as its capacity for removing iodine from solution. This relation is shown in Fig. 41. He extends the relationship when the substances to be adsorbed are of molecular dimensions

¹ J. Ind. Eng. Chem., vol. 15, p. 1252 (1923).

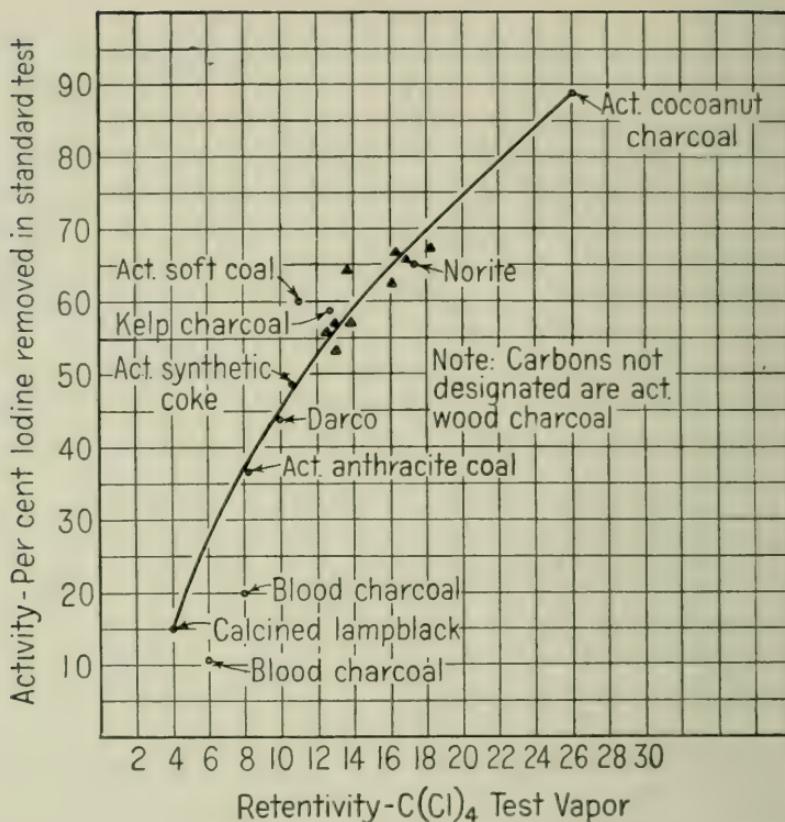


FIG. 41.—RELATIONSHIP BETWEEN "ACTIVITY" AND "REVENTIVITY" OF VARIOUS TYPES OF ACTIVATED CARBON

All carbons acid extracted, thoroughly washed, and dried before testing (Chaney)

by plotting the activity in terms of iodine removed in a standard test against the removal of a soluble oil by carbons of widely varying densities. This data is shown in Fig. 42. When the particles to be adsorbed are of colloidal dimensions, Chaney finds that all carbons of equivalent porosity or apparent density possess adsorptive capacities for colloidal particles directly proportional to their activity, as shown in Fig. 43. He tabulates a variety of technical and special carbons arranged in the order of diminishing decolorizing

power for a standard sugar solution. The table² is given below. The densities in column 1 and the activities in column 2 do not diminish with any corresponding regularity. If, however, we take the ratio of the values in column 2 to those in column 1, we find that they lie in a fairly smooth curve when plotted against decolorizing power. This is shown in Fig. 44. Chaney and his co-workers, therefore, reason that if the fineness of the carbon be a constant, adsorptive power of carbon for particles of colloidal dimensions

TABLE XX
COMPARATIVE DATA REGARDING VARIOUS ACTIVATED CARBONS
(Chaney)

Nature of Carbon	AD (200 to 270 Mesh)	Activity	Ratio of Activity to AD	Color removed from sugar soln., per cent	Ash Content per cent
	(1)	(2)	(3)	(4)	(5)
Activated wood charcoal	0.382	73.0	191	91.0	1.44
Activated coconut charcoal	0.548	95.0	173	90.0	0.83
Activated wood charcoal	0.426	64.0	150	89.4	2.30
Kelpchar	0.216	59.0	273	88.2	12.96
Norit	0.393	65.6	167	88.2	3.38
Activated soft coal	0.413	60.0	145	86.9	23.75
	0.472	67.5	143	86.8	2.97
	0.419	53.1	127	86.1	0.75
Activated wood charcoal	0.528	65.9	125	86.1	2.15
	0.376	46.5	123	85.3	1.32
	0.471	56.0	118	85.2	0.88
	0.503	58.5	116	85.4	4.03
Darco	0.470	44.0	93.6	85.7	30.00
Activated wood charcoal	0.570	57.0	100	83.3	1.74
	0.647	62.5	96	76.5	1.04
Activated coconut charcoal	0.766	72.9	93	62.3	2.14
Activated synthetic coke	0.714	48.5	68	33.3	9.19

All carbons pulverized to pass 200 mesh, acid-extracted, thoroughly washed and dried before testing.

is a function of the ratio of the activity to the apparent density, provided the carbon is of low ash content.

Manufacturing methods for the preparation of decolorizing carbons may be divided into several classes.

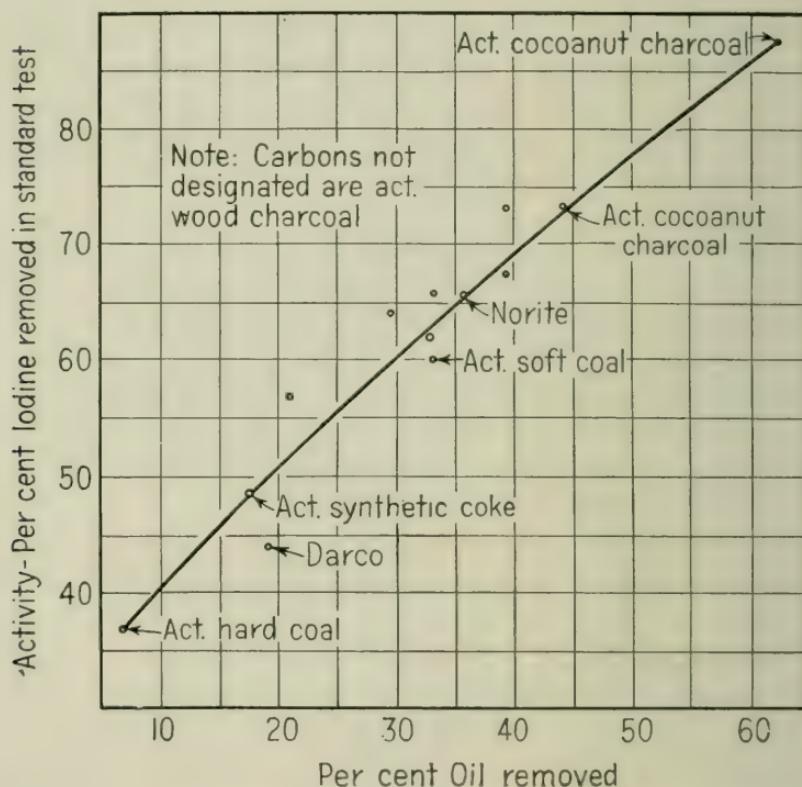


FIG. 42.—RELATIONSHIP BETWEEN ACTIVITY AND ALCOHOL PURIFYING POWER OF VARIOUS TYPES OF ACTIVATED CARBON

All carbons pulverized to pass 200 mesh screen, acid extracted, thoroughly washed, and dried before testing. Crude alcohol containing objectionable oil treated with 5 per cent carbon in the cold. Oil determination made by comparing turbidities on dilution by means of nephelometer (Chaney).

Class 1. Carbon may be deposited as a layer on a porous inorganic base. Carbonizable vegetable materials such as sawdust, seaweed, peat and molasses, as well as a large number of other materials may be mixed with porous substances such as infusorial earth, pumice stone, insoluble salts

and many other materials with or without the addition of a liquid binding medium. The mixture is strongly heated, whereupon the carbon in the vegetable matter is deposited throughout the porous base. Even as early as the middle

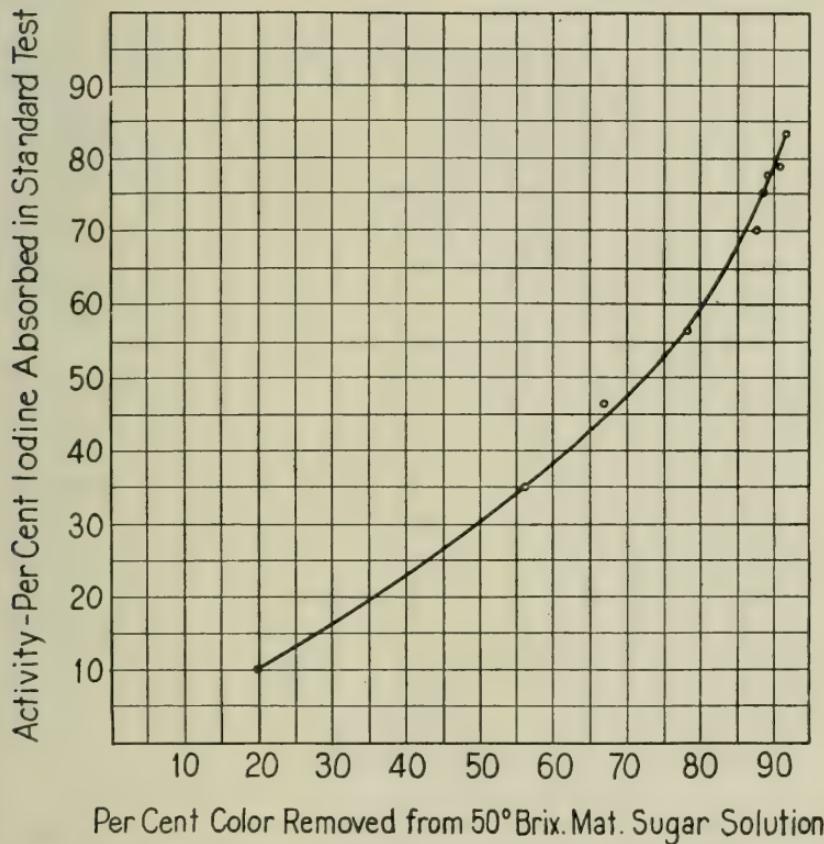


FIG. 43.—RELATIONSHIP BETWEEN ACTIVITY AND DECOLORIZING POWER OF ACTIVATED CARBONS FOR SUGAR SOLUTION

All carbons of approximately same apparent density, low ash content, and pulverized to pass 200 mesh. Five per cent carbon on basis of solids present used in decolorizing tests (Chaney)

of the last century there were constant endeavors to produce a nitrogenous carbon similar to bone char in which nitrogenous matters such as gelatin, casein, and albumen were added to the above mixtures. The nitrogen theory as ex-

plaining the action of bone char has been discussed under that heading. Sometimes instead of mixing vegetable substances with mineral materials, a natural high ash vegetable product such as rice hulls or husks containing an appreciable proportion of silica was used as a base material. An example

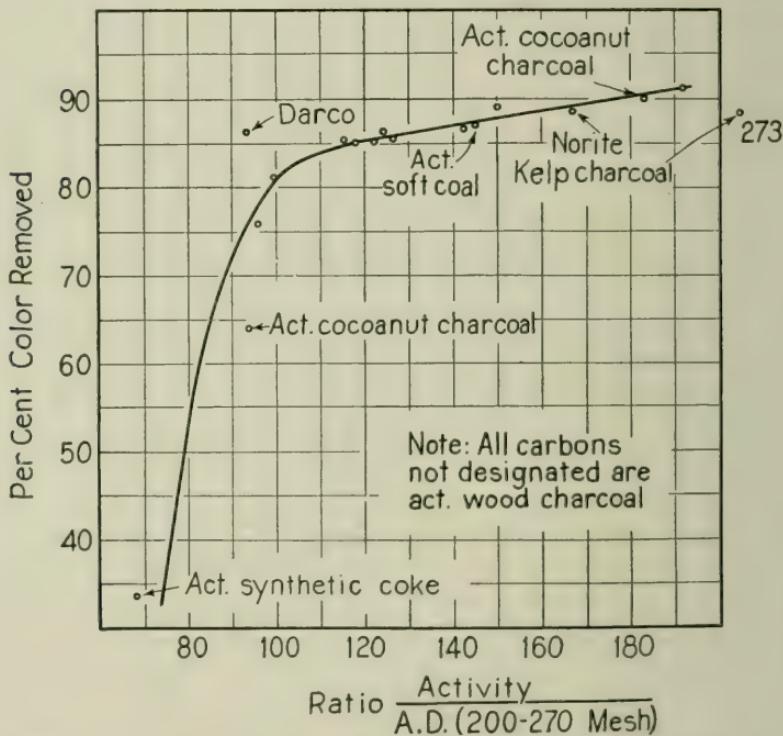


FIG. 44.—RELATIONSHIP BETWEEN RATIO OF ACTIVITY TO APPARANT DENSITY AND SUGAR DECOLORIZING POWER OF ACTIVATED CARBONS

All carbons pulverized to pass 200 mesh screen, acid extracted, thoroughly washed, and dried before testing. Ten per cent carbon on basis of solids present used in decolorizing a very dark 50° Brix mat. sugar solution (Chaney)

of this is the present day decolorizing carbon termed Carbrox. The object of the Class 1 process was to produce a material somewhat similar to bone char in that it had a porous structure with carbon distributed over a large area as well as appreciable mechanical strength.

Class 2. Carbon may be deposited on an inorganic base which is afterwards separated from the carbon by chemical means. Vegetable materials are mixed with chemical reagents such as lime, chalk, sulphuric acid, calcium chloride, zinc chloride, magnesium chloride, phosphoric acid and so forth, and after carbonization the inorganic matter is dissolved out, leaving the resulting carbon. The zinc chloride, phosphoric acid, etc., function as activating agents. Materials are usually carbonized at relatively low temperatures. Urbain ³ states that he considers zinc chloride acts first as a dehydrating agent exactly like sulphuric acid previously employed in carbon manufacture, and at a higher temperature during carbonization there is an abundant evolution of hydrochloric acid. This evolution is accompanied by the formation of zinc oxide. He states that it is to this zinc oxide that the final activation must be attributed, for he has demonstrated this by replacing zinc chloride by ammonium zincate. Ammonium zincate decomposes and loses its ammonia at a low temperature leaving only zinc oxide, in the presence of which the carbonization takes place. He states that the activation then obtained is almost exactly the same as with zinc chloride. As a result of his experimental work, Urbain employs phosphoric acid as an activating material, which, however, is recovered during the carbonization of the peat employed as a raw material. The commercial carbon termed Carboraffin, well known on the Continent but to a lesser extent in the United States, is made by the employment of zinc chloride as the activating material. Another method of manufacture consists of treating porous woods with dehydrating agents such as lime and calcium acetate, carbonizing them at nearly white heat under a layer of lime, cooling the mixture, giving the material an acid treatment with hydrochloric acid and recarbonizing a second time at red heat with the exclusion of air. The presence of the inorganic substances during carbonization of the mixture prevents the formation of the adsorbed films of inactive

³ *Recherches et Inventions*, #130, January 1926.

material which would cover the surface of the active carbon when they are adsorbed, as occurs when the vegetable materials are carbonized alone. Possibly gases evolved during the decomposition of the inorganic materials during burning assist in the formation of an active carbon. The exact nature of their action is not known. After preparation, the inorganic acids, bases and salts are removed by chemical treatment or by leaching.

Class 3. A number of important decolorizing chars are made by carbonizing materials such as lignite, waste pulp liquors, black ash residues, sawdust, woods and similar material in carbonizing retorts under controlled conditions of temperature and atmosphere. The desired porosities, compactness and mechanical strength of the resulting carbon will vary widely, depending upon the conditions under which it is initially carbonized. In some cases the material is given a second carbonization when in the form of carbon particles from which most of the volatile matter has been eliminated. After preparation the carbon is activated, in a manner similar to that described under gas-adsorbent carbons, by air, oxides of carbon, chlorine, superheated steam, or mixtures of steam and air. When gaseous compounds of carbon are used, carbon may be deposited therefrom in an active form on the material undergoing activation, especially if relatively low temperatures are maintained. The bulk density of the carbon particles is reduced somewhat during activation. Nuchar, for example, is made from paper mill waste liquors as a by-product in the recovery of the chemicals contained in these liquors. The material is carbonized under controlled conditions to determine its structural form and physical character. After carbonization it is heated directly by electric heat in a furnace wherein the carbon serves as a resistor between metallic electrodes. It is thus heated directly to the desired temperatures. After this secondary heating it is activated still further by gaseous (steam) treatment. Washing to remove soluble salts so as to allow the production of a neutral char may take place between the

first and second heatings or before activation or after activation, depending upon the effects desired. Darco, another industrial carbon, is made by the carbonization of lignite under definitely controlled conditions. According to the patent of R. W. Mumford,⁴ lignite is ground to 10 to 16 mesh and freed from all water-soluble matter. The mass is reduced to a paste by the addition of 1 to 15% of milk of starch or of gelatinous tricalcium phosphate, then 5 to 50% of 80 to 100 mesh dolomite is added and mixed to complete homogeneity. The mass is then heated progressively in rotating kilns vented to allow the escape of vapors. Porosity is imparted by the expulsion of water. The mass loses its plasticity and attains a permanent rigid structure after which drying and charring take place. The charring does not require the application of much external heat. Rapid rises of temperature are avoided by the mineral spacing agent which acts as an inert diluent. The main part of the charring is stated to take place at about 250° C., after which decomposition of the mineral spacing agent begins, the gases from which are taken up in the open pores of the adjacent particles of charred vegetable matter. The temperature is then increased to 800 to 900° C., after which the material is discharged into water with the exclusion of air. After preparation its high ash content is reduced by treatment with mineral acids such as hydrochloric acid and the material thereafter activated, usually by gaseous means such as air and steam. Norit, a Continental carbon, is made by the carbonization of birch wood⁵ and afterwards gas activated. Suchar is a twin sister of Nuchar, with the difference that the former is so manufactured as to give it the necessary physical properties to allow it to be repeatedly used and reactivated at periodic intervals, while Nuchar is made for a one-time use in most instances.

Most of the vegetable decolorizers appear in the form of black glistening powders. All of them are relatively soft

⁴ U. S. Patent 1,286,187 — 1918.

⁵ H. G. Tanner, Ind. Eng. Chem., vol. 17, pp. 1191-3 (1925).

chars. Their market form and characteristics vary widely, some of them being neutral, some acid and some alkaline. A large number of testing methods have been developed in an attempt to evaluate decolorizing carbons. Some of these base the evaluation on the relative amount of iodine removed from solution, others on determinations of the adsorption of ionized coloring material, such as ponceau red which is positive and methylene blue, the colored ion of which is negative. Caramel solutions have found favor with many. Some developments of this work have been described by Sanders,⁶ Zerban,⁷ Meade and Harris,⁸ Chaney,⁹ Teeple and Mahler,¹⁰ Blowski and Bon.¹¹ Most recent work tends to show that all adsorption by decolorizing carbon follows Freundlich's adsorption equation previously referred to under gas-adsorbent carbon. Teeple and Mahler found that within the range of commercial practice and within ordinary limits of error, this law holds for all carbons and solutions which they examined. They state that with a given Hess-Ives tint photometer and a given solution, the action of any carbon on that solution may be plotted logarithmically as a straight line and the comparative effectiveness of different carbons on that specific solution may be easily deduced.

In the present state of our knowledge, data regarding the action of carbons on one solution cannot be applied to a different solution but each one to be decolorized must be tested separately. The so-called standard methods of estimation have little practical value. The adsorption of color by carbon has been repeatedly shown to be a definite equilibrium reaction in which other materials than coloring matters assist or take part in the determination of the equilibrium.

⁶ Ind. Eng. Chem., vol. 15, pp. 784-5 (1923).

⁷ Ibid. vol. 12, p. 744 (1920).

⁸ Ibid. vol. 12, p. 686 (1920).

⁹ Ibid. vol. 15, p. 1244 (1923).

¹⁰ Ibid. vol. 16, p. 498 (1924).

¹¹ Ibid. vol. 18, p. 32 (1926).

The largest field of use for vegetable carbons is the sugar industry and similar manufacturing operations wherein decolorization is necessary. Carbons differ markedly in many of their characteristics. An acid carbon, for example, — that is, a carbon with a water extract that is decidedly acid, — will be a much better decolorizer; but a sugar refiner would never dare to employ a highly acid carbon despite its greater color removal, because of inversion of sucrose to non-crystallizable sugars with subsequent lowering of yield. The additional decolorizing value of the carbon would be more than offset by the losses involved through its use. The action of a vegetable carbon is very similar to that of bone char, but the material is very much more efficient. To obtain the same decolorizing value, from 1 to 5% (which latter is a very high figure) of a good grade of vegetable carbon will give the same results on the weight of the sugar handled as from 75 to 200% of good grade bone char. It is often pointed out that in comparison to bone char, the ash removal power of vegetable carbons as utilized in practice is small. This is partly due to the fact that ordinary vegetable carbons have no porous phosphate structure to aid in the removal of the soluble mineral salts. As in the case of bone char, the presence of abnormal quantities of uncrystallizable sugars in a sugar liquor reduces the decolorizing power of carbon, but the presence of an unusual amount of salts does not have this effect. Small quantities of a sugar dissolved in a liquor are adsorbed by decolorizing carbons. The carbon, however, has a very much greater adsorptive power for the so-called impurities in the sugar than for the dissolved sugar.

There must be intimate contact between the carbon when in use and the materials which it is to remove from the solution. The relatively large amount of bone char required makes it necessary to use this material in filters, as described under bone char. The char is held in place and the liquor passed through it. The relatively small amounts of decolorizing carbon necessary can be added to the clear

raw sugar liquors in mixing tanks or blowups. The decolorization of the liquor takes place very rapidly because the liquor comes in contact with the carbon surface almost immediately. With bone char several hours are required, as it takes time for the liquor to enter the pores of the phosphate structure and come in contact with the carbon. Vegetable decolorizing carbon, therefore, is carried through with the liquor, being removed by the use of various types of filters, for the operation and discussion of which the reader is referred to texts and articles on sugar manufacture. Many of the filters are of the Sweetland or leaf types, mechanically operated. The carbon remains on the cloths as a cake while the refined liquor passes out as a filtrate. In contradistinction to bone char practice in which the first effluents from the filters are very low in color and succeeding liquors become darker and darker, the whole of the refined liquor when vegetable carbon is used is of uniform color, because decolorization takes place before the mixture of liquor and carbon enters the filter. Another method of using vegetable carbons employs precoating of the filter cloths with a mixture of decolorizing carbon and water or with mixtures of decolorizing carbon, some sort of filter aid such as kieselguhr, Fuller's earth or celite, and water. After a layer or precoat has been formed the liquor is passed through the filter and in passing through the layer of carbon decolorization is effected. This method has the disadvantages of the bone char process in that the decolorizing carbon is not in contact with all of the liquor at one time and therefore the degree of decolorization of the liquor emerging from the filter steadily decreases as the decolorizing power of the carbon diminishes. In the first method a layer of carbon remains on the cloths of the filter but its decolorizing power has not been completely exhausted. In order to decolorize a further quantity of liquor, the layer may be left on the cloths and pre-decolorization done by passing liquor through the press as in the second method. In some cases the cakes are discharged from the filter into a fresh quantity of liquor

in the mixing vessel to effect some decolorization of new liquor.

There is no commercial method of decolorizing sugar liquor which does not involve the formation of a layer of carbon on the cloths of some type of filter. It is, therefore, essential that the carbon particles be of the correct size and structure to act as a good filter aid and permit a rapid rate of flow through the filter. Very finely powdered active carbon would have great decolorizing power, but the rate of flow through a layer of the carbon would be so slow that the use of the carbon would be decidedly uneconomic.

When a sugar liquor containing impurities comes in contact with a carbon, the attraction of the carbon for the impurities is greater than the attraction of the liquor for the impurities. The carbon therefore adsorbs the coloring materials until equilibrium is reached, after which point the decolorizing carbon will cause no further effects. At this point the mixture of sugar liquor and carbon is filtered. If this once used carbon is then introduced into a further quantity of the original or a darker liquor, further transference of the impurities from the liquor to the carbon would again take place until equilibrium is again reached. A smaller quantity of impurities is adsorbed by the carbon in its second use than in its first one, and the mixture may be passed through a filter and the carbon so separated used a third time. Theoretically, this practice can be repeated a very large number of times, but in actual practice decolorizing carbons are seldom used more than three times. The economic mechanical and operating factors determine in each case the manner of operating and the number of times that the carbon is used. By suitably decreasing the amounts of liquor (which is, in effect, increasing the percentage of carbon employed) with which the carbon comes in contact in each successive use, the percentages of impurities removed remain the same, so that one has three separate lots of liquor each one smaller than that which precedes it, but all decolorized to the same degree. Instead of using the decoloriz-

ing carbon a second or third time on clear raw sugar solutions, mother syrups darker than the liquor may be treated with the carbon previously used to decolorize raw syrup liquors. It is interesting to note that in the process specified in Derosne's patent of 1830, he stated that the charcoal was reduced to the size of fine gunpowder and then placed in layers on a cloth. In Martineau's patent of 1815, animal or vegetable charcoal in the form of a powder was added to the liquor which was then passed through a cloth filter. It is thus seen that vegetable carbons and the present means of using them are by no means modern inventions. Efficient means for activating them during manufacture and revivifying them after use are only recent developments.

When carbon has been used for the last time prior to revivification, the cakes remaining on the cloths of the filters have to be sweetened off or washed. Most of the liquor remaining in the chambers of the press and in the cakes is forced out with air under pressure before the wash water is admitted. In contradistinction to the operations employed in a bone char plant, when vegetable carbons are used there is practically no light liquor because the wash water effluent rapidly falls to a low sugar concentration corresponding to that of the char water from a bone char filter.

Vegetable carbons tenaciously retain adsorbed coloring matters and impurities which are not given up to the wash water as in the case of bone char. When cakes of the usual carbons are sweetened off, the purity of the wash water does not fall below 95. This allows all the wash water to be used for melting raw sugar with the subsequent avoidance of the use of steam for evaporation of the wash liquors. No heated water is therefore lost down the sewer. Despite the fact that a greater quantity of water may be required to sweeten off a given weight of decolorizing carbon than is required for an equal weight of bone char, the amount of wash water per ton of sugar is very much less with decolorizing carbon. This is due to the fact that the amount of de-

colorizing carbon for the same effective decolorization is only a very small percentage of the bone char that would have to be employed to do the same work.

It has often been pointed out that the amount of sugar decomposed in the pores of bone char during sweetening off and washing is greater than the quantity of sugar so lost

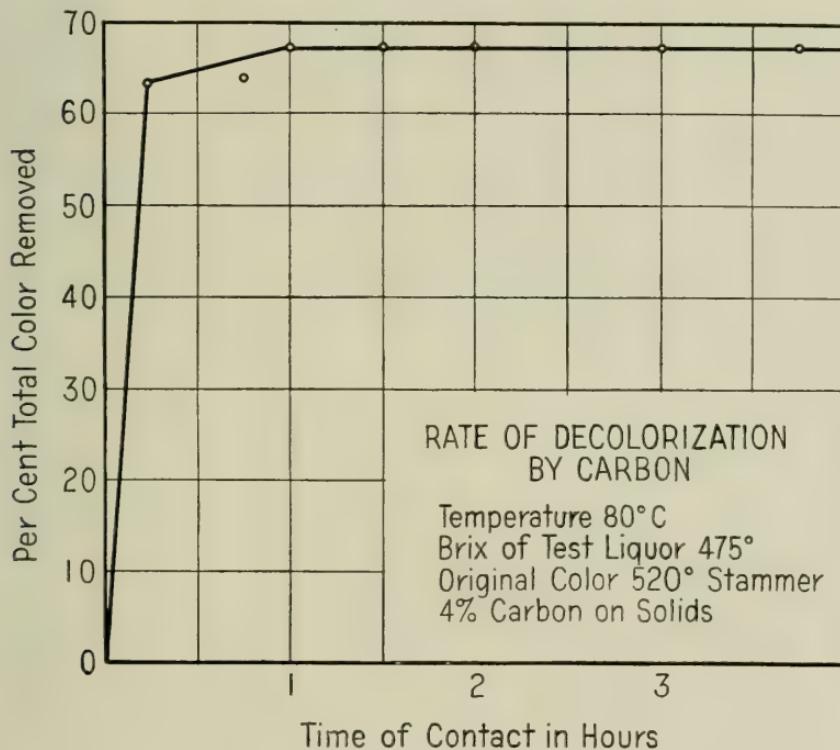


FIG. 45.—RATE OF DECOLORIZATION BY CARBON
(Blowski and Bon)

when the same operations are done on vegetable carbon cakes. Some authorities claim that at least one ton of sugar is lost by decomposition for every 100 tons of bone char used. With decolorizing carbons the loss is negligible.

There are a large number of factors to be taken into account in the use of decolorizing carbons in the sugar in-

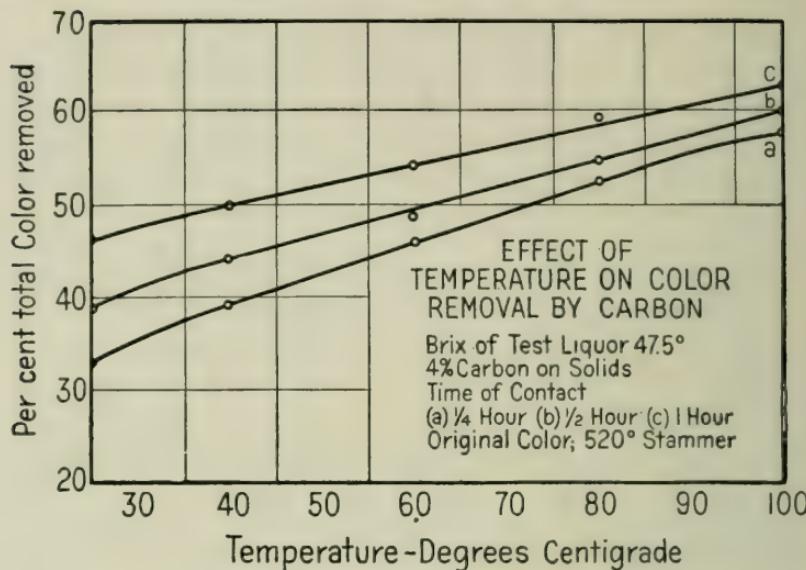


FIG. 46.—EFFECT OF TEMPERATURE ON COLOR REMOVAL BY CARBON
(Blowski and Bon)

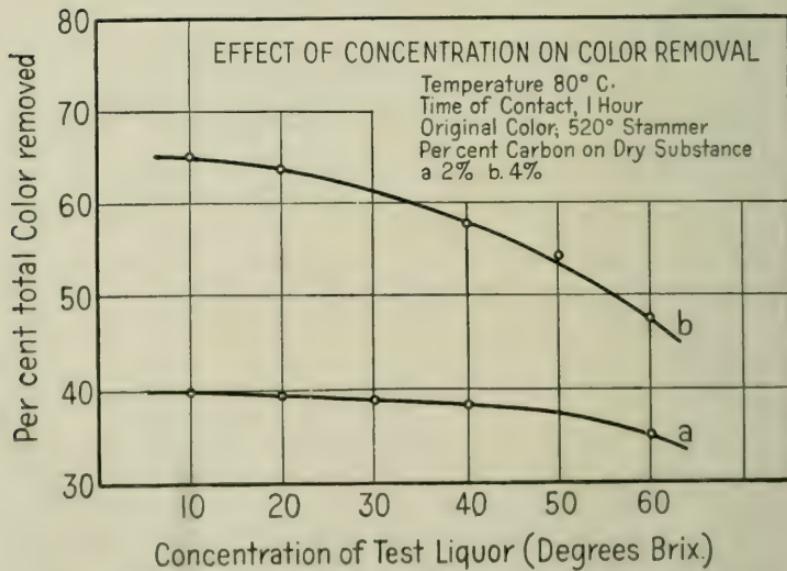


FIG. 47.—EFFECT OF CONCENTRATION ON COLOR REMOVAL
(Blowski and Bon)

dustry. The rate of adsorption, as shown by the observations of many investigators, of the color from a sugar solution is very rapid during the first interval of contact and gradually reaches a point where increased time of contact results in no further decolorization. This indication of saturation is shown in Fig. 45. There is increased color removal at higher temperatures when only one type of color removal is considered. This is indicated by the curves in Fig. 46. The percentage of color removal varies inversely with the concentration of the test liquor, as shown in Fig. 47. When time of contact and temperature are fixed, the percentage of total color removed varies directly with the percentage of carbon used, as shown in Fig. 48. These observations will be general for all carbons, the curves varying slightly with the characteristics of the individual carbons.

The characteristics of commercial decolorizing carbons will be largely the result of their raw materials and the processes used in their manufacture. As an example, Norit will run about 95% carbon, 4.5 to 6.5% ash of which 2.3% is hydrochloric acid soluble. Its water extract shows a pH of 7.8 to 8.3. It is stated by its manufacturers to contain a small percentage of slightly soluble ash which imparts the alkaline reaction. This ash is best removed by digestion with one per cent hydrochloric acid prior to use. Darco runs from 68 to 70% carbon, 30.5% ash of which about 0.5% is hydrochloric acid soluble. The water extract shows a pH of from 4.5 to 6, which is presumably a residual acidity from treatment with the acid solvent after carbonization. Carbrox shows a carbon percentage of about 94, an ash content of 6.5% of which approximately 0.5% is hydrochloric acid soluble. The pH of its water extract varies from 6.5 to 7. Suchar has a carbon content of 97 to 99%, an ash content of 2.0 to 3.5%, of which two-thirds is hydrochloric acid soluble. Its water extract pH is from 6.3 to nearly 7. Nuchar has similar characteristics. Carboraffin runs 84 to 87% carbon, 3 to 4% ash with traces of zinc oxide and considerable percentages of oxygen and nitrogen.

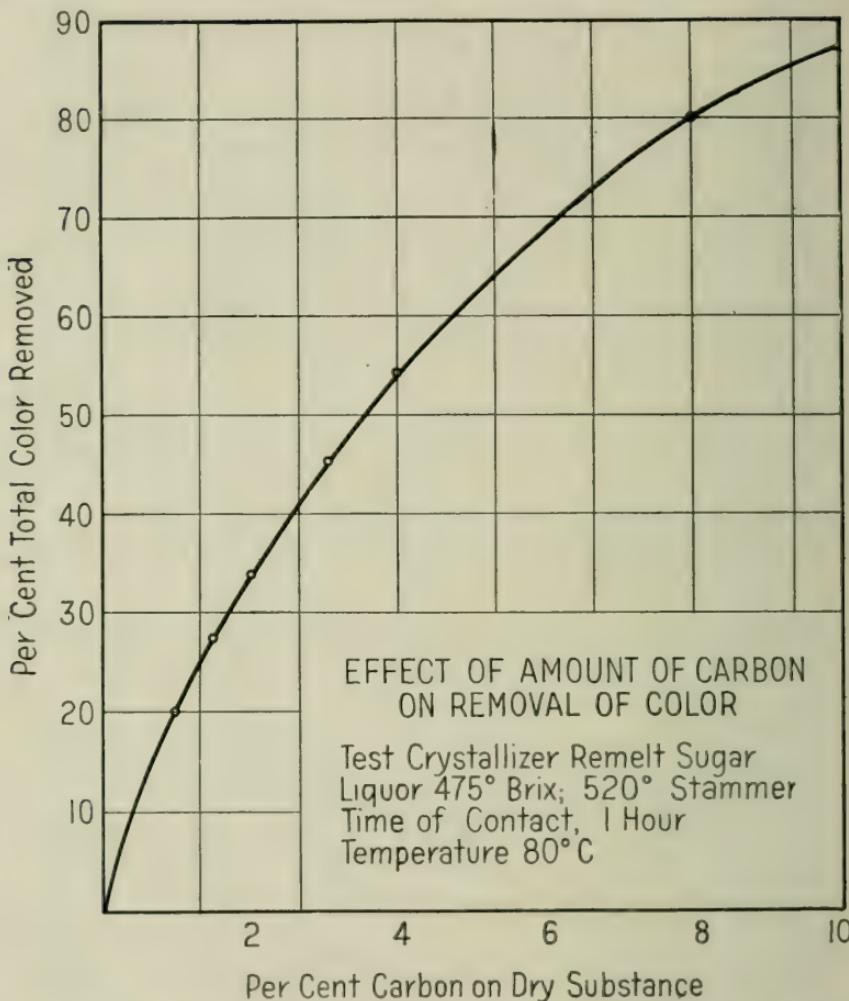


FIG. 48.—EFFECT OF VARIATION OF AMOUNT OF CARBON ON COLOR REMOVAL
(Blowski and Bon)

It is decidedly acid, and in practice limestone has to be added during its use. For purposes of comparison, new bone char will run from 9.5 to 10% carbon, the remainder being ash practically all of which is hydrochloric acid soluble.

The acid or alkaline reactions of these chars cannot be neutralized by washing alone. Weak alkaline solutions

followed by thorough washing are necessary to neutralize the acid carbons, and weak acid solutions need to be employed to neutralize the alkaline carbons. Hauge and Willaman¹² show that the more acid a solution is the greater is the adsorption of caramel, negatively charged color bodies and colloids, while alkalinity favors adsorption of electropositive substances such as colors of the methylene blue type. The adsorption of amphoteric substances such as proteins, is at a maximum in the general region of the isoelectric point of the protein, and is at decided minima in the extremes of

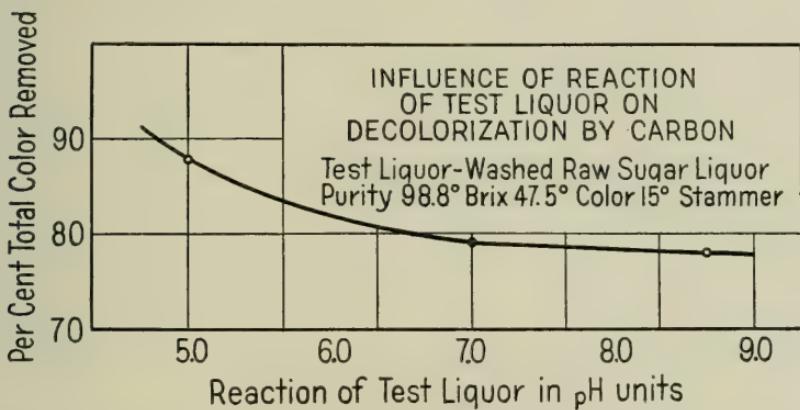


FIG. 49.—EFFECT OF pH ON DECOLORIZING
(Blowski and Bon)

alkalinity and acidity. Adsorption of non-electrolytes, such as sugars, is not affected by pH. Most colored materials met in industry are negatively charged, and their decolorization will vary inversely with the pH of the solution as in Fig. 49.

Physically, the commercial decolorizing carbons vary considerably in their weights per unit volume and their screen analyses. Table XXI shows the weight per cu. ft. of the carbons and their screen analyses on the standard Tyler screens. There is a wide variation in the fines,—

¹² J. Ind. Eng. Chem., vol. 19, #8, p. 943 (1927).

that is, material going through the 200 mesh screens. When Norit is examined under the microscope, it is seen to con-

TABLE XXI

Carbon	Loose Pack Lb. / cu.ft.	Solid Pack Lb. / cu.ft.	SCREEN ANALYSIS — %					
			On 50	On 70	On 100	On 150	On 200	Thru 200
Suchar	10.5	13.5	7.1	20.5	11.7	13.8	14.2	32.7
Norit	14.0	18.4	0.2	7.2	11.1	14.5	12.7	54.3
Carbrox	16.0	19.2	0.4	1.3	8.4	20.5	38.9	30.5
Darco	17.9	22.5	1.6	7.9	13.2	16.5	20.3	40.5

sist of innumerable needle-like carbonized vegetable fibres. Darco and powdered bone char have a somewhat granular structure, while Carbrox, Suchar and Kelpchar are very flocculent powders. Carboraffin is ground exceedingly fine. Its screen analysis would show a much greater percentage on and through the 200 mesh than the average commercial carbon. Blowski and Bon¹³ find as a result of their studies



FIG. 50.—RELATIVE SIZES OF GAS ADSORBENT AND DECOLORIZING MATERIALS

on ash adsorption, that a number of commercial decolorizing carbons on a weight for weight basis have decidedly higher ash removal powers than normal bone char. This is

¹³ J. Ind. Eng. Chem., vol. 18, p. 37 (1926).

quite interesting in view of the number of times the statement has been made that synthetic vegetable chars are inferior to bone char in ash removal powers. It is stated, however, that the ash adsorbed from sugar solutions by decolorizing carbon in actual practice was very small, due to the small percentages of carbon used in the treatment. Sugar operators as a result of bone char practice have found that every pound of ash eliminated from sugar liquors has meant an increase of approximately $2\frac{1}{2}$ lbs. of sugar recovered through crystallization. It is interesting to note that when bone char is sweetened off or washed, a large part of the ash is washed out of the char and returns to the sugar liquors with the sweet water. In other words, some ash is never removed from the system and merely circulates continuously. The net result is that the sugars made with vegetable carbons contain no more ash than those made with bone char. The ash which is removed from the sugar liquors by vegetable carbons is taken completely out of the system during the periodic acid washing of the carbon. The essential criterion, however, in comparing bone char sugar refineries and vegetable decolorizing sugar refineries is found in the percentage of sugar recovered, — that is, the number of pounds of finished sugar as compared to the number of pounds of sugar in the raw liquors. It has been determined by common bone char refinery practice that 93 lbs. of standard granulated sugar should be produced from every 100 lbs. of 96° test raw sugar melted. Present day recoveries in refineries in the tropics employing vegetable carbons show 93.5 lbs. or better of standard granulated sugar from every 100 lbs. of 96° test raw sugar melted.

The removal by carbon of colors in solutions varies widely. Given the same carbon with different varieties and types of colors, the adsorption isotherms will be markedly different. An example is given in Fig. 51, wherein decolorization was studied with the same carbon but applied to different types of sugar liquors. Liquor A was washed raw sugar liquor of 98.8° purity with a color of 18° Stammer

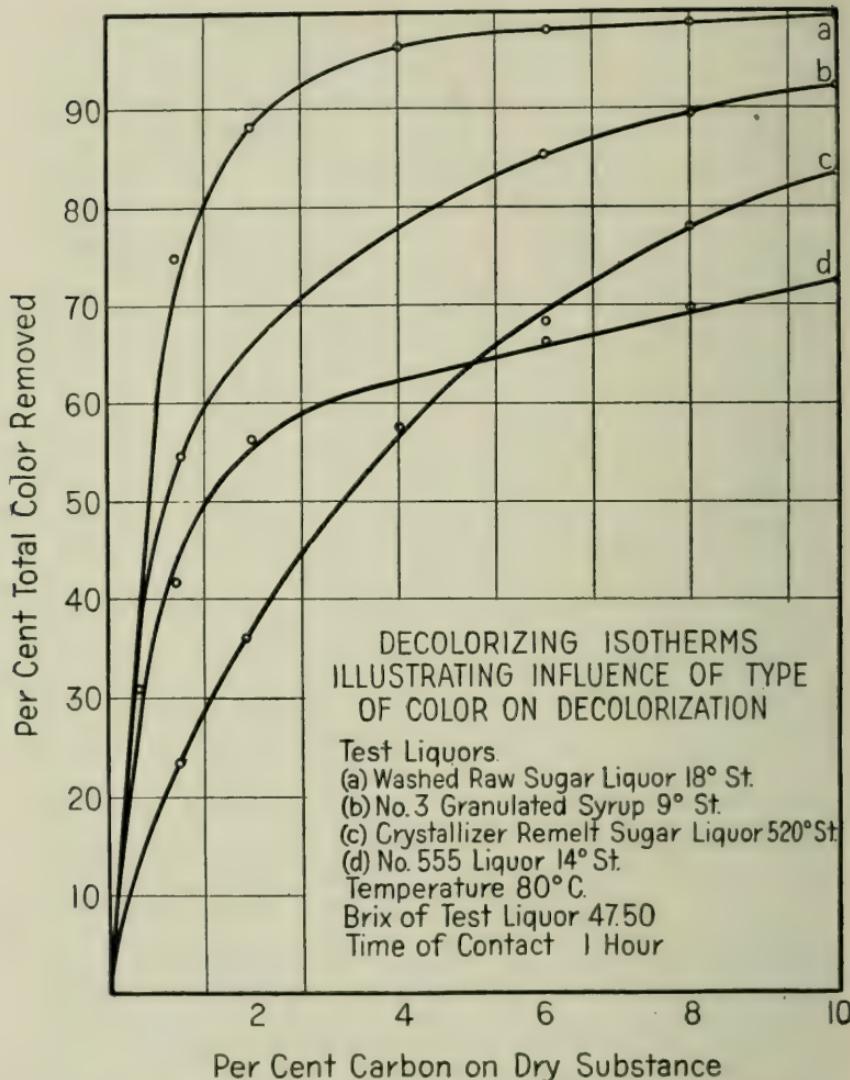


FIG. 51.—INFLUENCE OF TYPE OF COLOR ON DECOLORIZING
(Blowski and Bon)

per 100° Brix; B was a granulated syrup with a color of 9° Stammer; C a crystallizer remelt sugar liquor of 88.5° purity with a color of 520° Stammer per 100° Brix; D was

a very highly char filtered liquor with a color approximating that of washed raw sugar liquor. All observations were made at a temperature of 80° C., the density of the liquor being 47.5° Brix and the time of contact one hour. The color in the washed raw sugar liquor was readily removed with a small percentage of carbon. The decolorization of the crystallizer remelt sugar liquor was considerably more difficult than that of the washed raw sugar liquor. With the highly char filtered liquor, a sharp break occurred between 50 and 60% decolorization instead of at 90% as with the washed raw sugar liquor. This seems to indicate that the liquor contains two types of coloring matter in approximately equal quantities, one of which is comparatively readily removed by carbon and the other of which is removed with difficulty.

When the various vegetable carbons are compared on an equal weight basis on the same type of sugar, the curves as given in Figs. 52 and 53 show them all to be not widely different in their effective action. All of them, however, have markedly greater decolorizing powers than either highly acid washed bone char, running 98.5% carbon, or new ground bone char, or granular new bone char. Fig. 52 gives the data when the tests were made on washed raw sugar liquor, and Fig. 53 on crystallizer remelt sugar liquor.

The value of any vegetable carbon used for decolorizing does not depend alone upon its decolorizing efficiency but upon a number of other factors in addition. At times its decolorizing efficiency may be the least important of its properties, as this factor may be outweighed by other characteristics of the carbon. As has been pointed out before, a low pH carbon would be a more effective decolorizer, but a sugar manufacturer would not use such a material because of the inversion losses it would cause, due to its acidity. A proper carbon should have high efficiency as a filter, and not require additional materials such as Filter-Cel, kieselguhr, or Fuller's earth to aid in filtration, for these would interfere with the regeneration of the carbon. Many de-

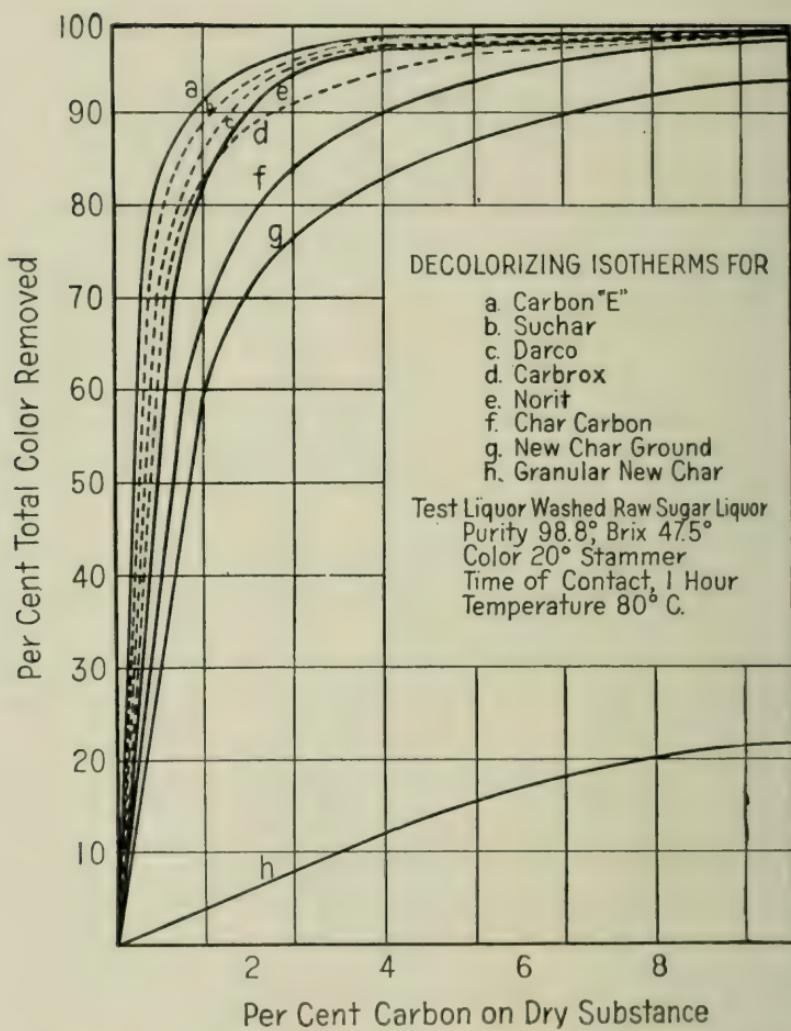


FIG. 52.—COMPARISON OF EFFECT OF VARIOUS VEGETABLE CARBONS ON WASHED RAW SUGAR LIQUOR
(Blowski and Bon)

colorizing carbons are very effective in their color removal action, but are not readily revivified. Some of them may require acid or chemical treatment to put them back in their former condition. It has only been in recent years

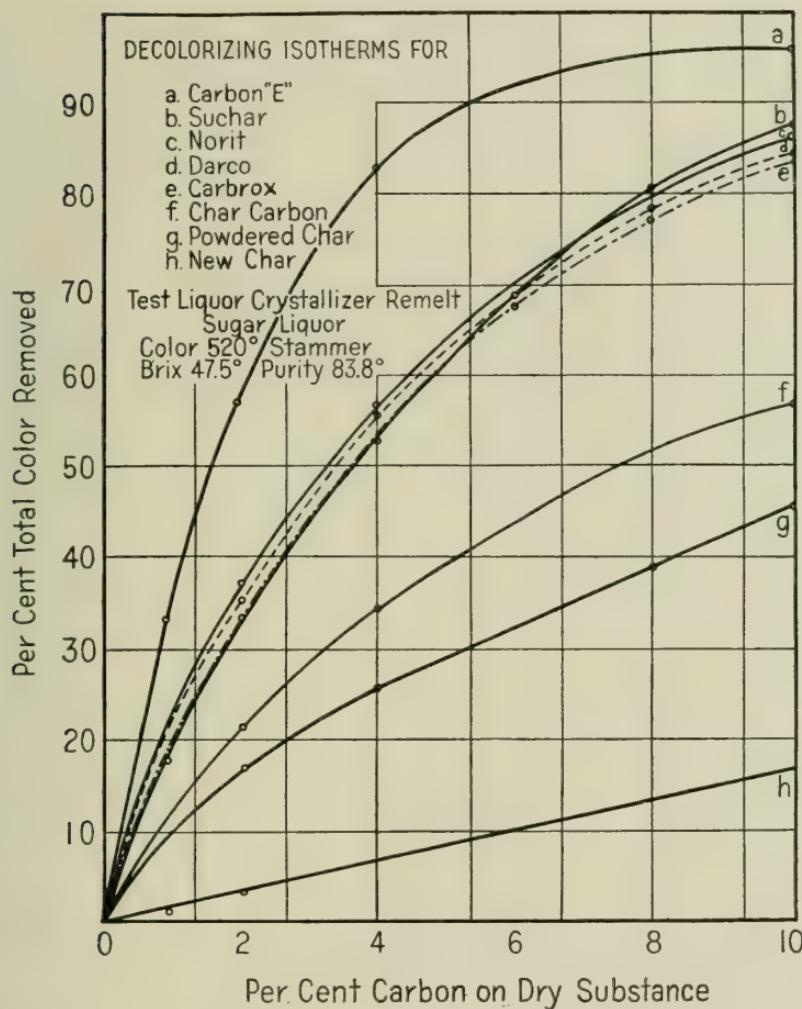


FIG. 53.—COMPARISON OF EFFECT OF VARIOUS VEGETABLE CARBONS ON CRYSTALLIZER REMELT SUGAR LIQUOR (Blowski and Bon)

that commercial types of revivifying furnaces for vegetable carbons have been developed. At times, low unit cost of the material may be of importance. In continued use, mechanical strength, resistance to crushing and dusting of

the carbon are necessary characteristics. Some decolorizing carbons are made and sold relatively cheaply for a one-time use, — that is, they are to be used once and discarded. Others, a notable example of which is Suchar, are specifically prepared for continuous use, ready filtration and adaptability to revivification.

In the refining of raw sugar there are three types of impurities to be eliminated: (1) solid suspended matter, (2) gums, ash and other non-sugars in solution, and (3) soluble coloring matter. The first step in the refining process is the washing of the raw sugar, which separates it into a washed sugar of 98.5° to 99° purity, subsequently melted to a liquor of 60 to 65° Brix, and a low grade syrup of about 80% purity which contains most of the non-sugars of the original raw sugar.

In the bone char process of refining, these liquors are clarified by a cloth filtration and then filtered over bone char. The char decolorizes the high purity liquors and removes a large part of the color and soluble non-sugars from the low grade products. This elimination of non-sugars, commonly amounting to about 1% of the melt, results in a reduced molasses production. The use of decolorizing carbons as a substitute for bone char in sugar refining has made considerable progress in recent years.

The bone char process, established as the standard process for the refining of sugar, has the advantages that the material is easily regenerated; the replacement of char due to shrinkage and dust is small, amounting to 13 to 15% per annum of the char in process; and the procedure has a highly developed technology. There are, however, a number of disadvantages, such as the large investment in plant, the large amount of material to be handled, and the large wash water consumption with its attendant large fuel cost for recovery of materials in the wash water. It is often stated by bone char operators that vegetable carbons do not remove non-sugars from solution. This matter has been

discussed previously. Paine and Badollet¹⁴ show that the reversible colloids taken up by bone char are almost completely washed off when the char is "sweetened off." The capacity which bone char possesses for adsorbing these colloidal non-sugars is limited. If the colloidal matter which has been removed by the bone char is returned to the process at the beginning of the next cycle, it follows that the colloidal removal on the second cycle will be less than on the first. The colloidal non-sugars will then only circulate in the system to a large extent since the "sweet water" goes back into process. Vegetable decolorizing carbons have the advantages of a simple process with reduced inversion losses, a small investment and a small wash water requirement. The disadvantages are losses in regeneration of a higher amount than those of bone char, and as yet a technology which is young and capable of considerable development. The loss of carbon on revivification of a vegetable carbon with a good type of revivifying furnace, is stated not to exceed 5% per cycle. It would be exceedingly interesting to compare on an economic basis the cost of carbon and bone char, per unit weight of sugar produced, used in the same type of plant, when the facts that the decolorizing carbons cost from $3\frac{1}{2}$ to 4 times the unit cost of first grade bone char, that the losses in regeneration are higher than those of bone char, but that the efficiencies on a weight basis of vegetable carbons are many times that of the best grade of bone char, are considered.

Commercial revivification of vegetable decolorizing carbons has been developed by the manufacturers of Norit and Suchar. Inasmuch as the equipment and processes involved are essentially different, they will each be described. The Norit kiln is in principle the same as that employed for bone char. Its construction differs inasmuch as fine powders have to be handled instead of large granules. In place of the vertical drying and burning pipes, horizontal troughs fitted with spiral conveyors are employed to dry

¹⁴ Facts about Sugar, Jan. 15, 1927.

the carbon. The material then falls into horizontal revivifying retorts through which it is moved by spiral conveyors. The revivifying retorts themselves are essentially large diameter pipes ordinarily made of cast iron. Coal, coke or fuel oil in a furnace is used for heating, the products of combustion passing around the retort pipes. Considerable difficulty is encountered in kiln revivification of vegetable decolorizing chars inasmuch as they ordinarily show poor thermal conductivity. The heat is applied outside of the pipes and the insulating effect of the fine carbon makes uncertain the ensuring of correct revivification temperatures in the carbon itself. The carbon is automatically fed into the pre-drying troughs where it is heated to about 400° F. It then falls into the upper revivifying retorts where the temperature is raised to 650° F. After discharge, it falls into the bottom retorts where the temperature reaches 1000° F. During the burning, the coloring matter and other organic impurities such as gums which have been adsorbed from the sugar liquor are carbonized. The gases resulting from the decomposition of the impurities are vented off. The hot revivified carbon, after discharge from the last retort, falls into a water tank situated underneath the kiln. This avoids the use of cooling pipes, carbon oxidation, and the loss of carbon dust which would result if the material were handled dry. The carbon produced by the decomposition of impurities has little if any decolorizing power. During regeneration the carbon may be activated and the deposited carbon removed by the admission of superheated steam or air under properly controlled conditions into the revivifying retorts. Synthetic vegetable carbons, such as Norit and others, retain with great tenacity mineral salts that they have adsorbed. These are not given up during sweetening off and washing, nor are they removed in revivification. The mineral salts are removed by dilute hydrochloric acid (2%) and boiling water. Cakes of carbon are added to the vat until the mixture contains about 20% of Norit and the whole agitated by stirrers for about an hour. The acid dissolves the mineral

salts, and the gums which may have been adsorbed from the clear raw sugar liquor are changed by the acid into readily soluble compounds from which the carbon is separated by filtration. The cakes of the carbon are washed in the filter press with fresh water and, if reburning does not follow, with a weak alkaline solution of soda ash followed by a second washing with fresh water. The acid wash is applied after about every six cycles of use and revivification.

Burning kilns present the difficulties of maintenance of proper temperature, successful venting of gases, and efficient removal of the inactive deposited carbon by burning. In order to eliminate these difficulties there has been developed in the United States an electrical revivification method which has specific application to the use of the carbon termed Suchar. In the manufacture of Suchar, one step in the process imparts to the carbon the property of high electrical conductivity and at the same time low thermal conductivity. Advantage is taken of this property of high electrical conductivity to revivify the Suchar by subjecting the carbon to the action of an electric current. The furnace, as shown in Fig. 54, consists essentially of three parts: a hopper for measuring the charge, a revolving tank lined with fire-brick constituting the furnace proper, and a water tank below for receiving and quenching the revivified carbon. Suspended from the cover on top of the furnace are the electrodes for electrifying the carbon. They consist of iron plates set in an insulated base at a sufficient angle to act as plows to agitate the carbon as the revolving furnace brings it in contact with the electrodes. The furnace voltage is ordinarily low, the maximum value being 100 volts. The furnace is designed so that each particle of carbon is brought repeatedly in the path of the electric current. Small arcs between the carbon particles are formed and the carbon is rapidly heated to the temperature necessary for revivification. Furnace power consumption is of the order of 200 k.w.h. per ton of carbon revivified.

After being heated the proper length of time for revivifi-

cation, the material is dumped from the furnace into the water tank below. There has recently been developed a commercial operating unit of a continuous electrical revivifying furnace. This furnace is horizontal with an interior arrangement allowing the carbon to pass through continu-

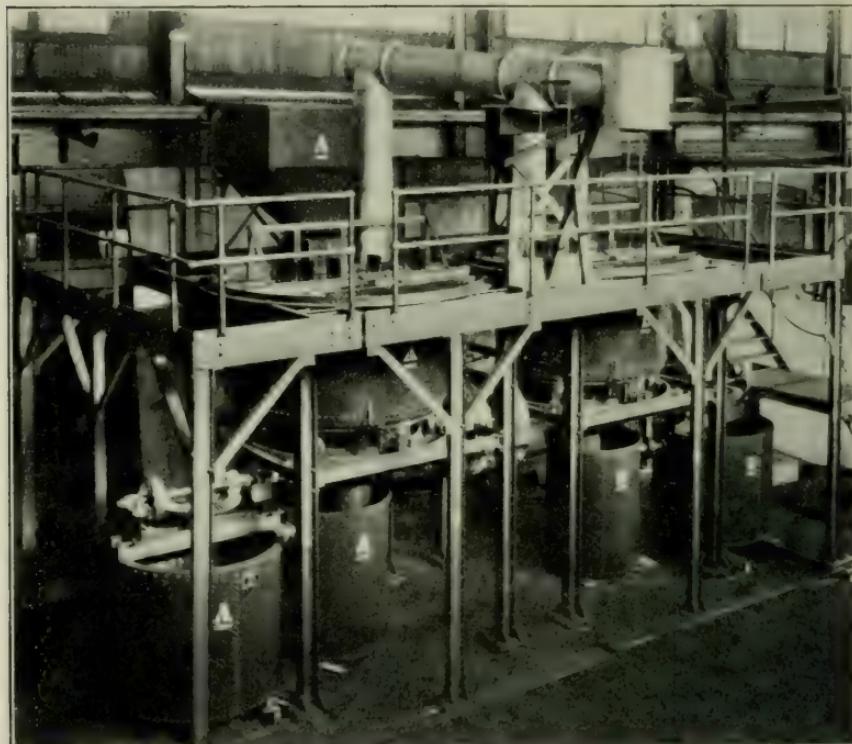


FIG. 54.—THE WINDOK FURNACE USED FOR CARBON REVIVIFICATION
(Courtesy Suchar Process Corporation)

ously while being electrically heated. It represents considerable advance over the batch furnace.

If it be found necessary, at periodic intervals acid washing of the carbon is done in the same manner as described previously for Norit.

Decolorizing carbons find a large number of applications in industry on a one-time use basis. They are widely em-

ployed in the manufacture of chemical, pharmaceutical and food products, appearing in the market either as solids, liquids or solutions.

In the manufacture of pure solids, especially water white solids, the last stage in the process is usually their crystallization from some solution. Should the solution be colorless and brilliant, no trouble is experienced in obtaining crops of water white crystals. If, however, the solution be colored, the resulting crystals will probably be contaminated with this color, in spite of the fact that the greater part of the coloring matter will remain behind in the mother liquor. To produce the highest grade product it is then necessary that the crystals be redissolved and the crystallization process repeated as many times as needed to obtain a pure product.

Decolorization of the original liquors by means of vegetable carbons effects in most cases complete removal of the color, or the production of liquids for crystallization of a color and appearance that will give satisfactory crystals on concentration. The treatment is simple, rapid and inexpensive, as it minimizes the number of necessary operations to produce a product of the required quality. Greater recovery of crystals from solution is obtained because of the elimination of losses in the various mother liquors incidental to repeated recrystallization.

Other than sugars, decolorization by carbon has been successfully applied to the manufacture of tartaric acid and tartrates, citric acid and citrates, salicylic acid and salicylates, quinine salts, caffein and similar alkaloids, as well as a large number of drugs such as acetanilide and related products. Depending upon the amount of color, the solutions are treated with relatively small percentages of carbon, being as low as 0.25% in easily decolorizable materials to as high as 4 to 5% in difficult cases. As has been stated before, each new material to be decolorized is a specific problem by itself, necessitating study as to the proper amount of carbon, the specific effects of the various commercial varieties with resultant definite adaptability of some in preference to others.

The carbons in the form of fine powders are effectively stirred into the solutions to be decolorized, allowed to remain in contact for some time and then filtered out of the solution.

Carbon decolorization has been applied to a number of inorganic materials such as borax, epsom salts, Glauber's salts, boric acid and related products. After decolorization and filtering, the clear mother liquors are crystallized.

Gelatin is often produced in a clear colorless state through the use of vegetable carbons. Similar processes are applied for the bleaching of resins and gums by treating them with carbon in suitable solvents. Their colors and purities are appreciably improved.

In some cases it has been found very difficult to prepare crystals of satisfactory color by repeated crystallization, because of the susceptibility of the solution to chemical changes within itself, or due to oxidation by air. The manufacture of such products as gallic acid has been much facilitated by decolorizing with vegetable carbons and limiting the crystallization to a single operation.

In decolorizing and sometimes deodorizing liquid products, the usual procedure has been to distil the liquid with or without some previous chemical treatment, leaving the coloring matter and impurities behind in the still. This method is not only expensive in general but must be performed in many instances under conditions that make it more costly. This is due to the appreciable loss of product involved in the operation, owing to the fact that some material must be left in the still to prevent any of the color and impurities passing over to the condenser.

In the dry cleaning industry, various petroleum solvents such as gasoline, naphtha, etc., are used to remove dirt, greases and stains from clothes, carpets, and various fabrics. The solvent becomes highly contaminated after repeated use and eventually is so highly colored and saturated as to be unfit for further application as a cleaning material. There has been much work done recently in the application of decolorizing carbon for recovery of these highly contaminated

solvents. Steam distillation, at least with the type of equipment now used by dry cleaners for distilling batches of dirty solvent, is far too costly for use as a continuous decolorizing process. It is also seriously handicapped by the fact that relatively large quantities of steam and cooling water are needed for the recovery of the distilled product. Certain chemical processes, such as those employing caustic soda washes for the dirty solvent, have been used; but it was found that this method did not prevent the slow accumulation of color and odor in the continuously re-used solvent.

Work instituted at the Bureau of Standards in 1924 by the National Association of Dyers and Cleaners¹⁵ demonstrated that used cleaners' solvent could be reclaimed by the use of certain types of decolorizing carbons in connection with aqueous alkaline solutions. Although this process was originally proposed for treating batches of contaminated solvent, it was soon found that it could be readily applied in continuous systems.

The decolorizing carbon process for removing solvent contamination is essentially suitable for operation on the continuous rather than on the batch system, in that the cost of completely decolorizing a volume of badly contaminated solvent is quite high, while the cost of removing, more or less completely, a small amount of color from a large volume of solvent is low.

Almost all of the commercial carbons are suitable for this work and equipment for the purpose is on the market. At times revivification of the carbon may be made, although ordinarily the product after saturation with color is replaced by new material.

Similar uses of decolorizing carbon have been made in connection with the purification of glycerine, gasoline and other hydrocarbons, various solvents and alcohol.

Dudley,¹⁶ as a result of his experiments with the action of carbon on different whiskies, states that the soluble consti-

¹⁵ Hubbard: Bureau of Standards Tech. Paper #280, 1925.

¹⁶ J. Amer. Chem. Soc., vol. 30, pp. 1784-9.

tuents are removed to some extent by adsorption, but mostly by diffusion into the particles of charcoal where the liquids of higher molecular weight are held longer than those of lower molecular weight. When charcoal filters are used, the length of the column of charcoal and the size of the particles, the density of the packing and the speed of the filtration are important factors. If the flow of the liquid is too rapid, the proportion of the constituents of higher molecular weight which are adsorbed by the charcoal is small, and therefore little is removed. If the flow is too slow, they will be given up by diffusion out of the charcoal into the whiskey. If the liquid remains in contact with the charcoal long enough, only the very small amount of materials adsorbed will be removed from the whiskey. Furfurol is completely taken out by charcoal. The same applies to the fatty and essential oils in solution. Vlenski and Humnicky¹⁷ state the content fusel oil of crude spirits decreases considerably as the result of char filtration, but that the content of aldehyde, on the contrary, increases unless the crude spirit contain very much aldehyde. The amount of esters is diminished and the acids of the crude spirit are neutralized by the alkaline content of the charcoal. Wuorinen and Lauren,¹⁸ in their study of the of action of birch charcoal used in the purification of ethyl alcohol, find that only formaldehyde, out of a large number of aldehydes studied, was not removed by the charcoal. Unsaturated aldehydes are readily removed by adsorption, and the amount of formaldehyde removed is dependent upon the quantity of the charcoal used.

Decolorizing carbon has been successfully applied to a number of products which appear on the market in different concentrations and of a color and purity which bear a strict relation to their selling values. This holds true quite definitely for phosphoric and lactic acids. In the latter case, whether it be prepared chemically or by fermentation, carbon decolorization is used almost exclusively in the purification of the product.

¹⁷ Z. Angew. Chem., vol. 31, pp. 1639-46 (1908).

¹⁸ Ann. Acad. Sci. Fennicae A., 24, #2, pp. 3-10 (1924).

In some cases, particularly food products such as cider vinegar or industrial materials like acetic acid, decolorizing carbon is employed not only to remove color but also to eliminate flavors and odors which are quite detrimental to the selling value of the product. This also applies to pectins and fruit juices made from all manner of fruits where the material to be removed is of a colloidal nature and granular carbons are used. The granular carbons are being displaced by powdered carbon and kieselguhr as a filter aid.

The standard bleaching material used by oil refiners has long been Fuller's earth, a clay which has to a limited extent the same adsorptive properties for impurities as synthetic vegetable carbons. Because of its comparative cheapness, large quantities may be used without making the cost of bleaching inordinately high. The use of such large quantities in the past has given results which made its continued use acceptable. Fuller's earth, however, has only a limited decolorizing power. Its use entails a number of disadvantages which have led the vegetable oil refiners to make radical changes in recent years in their bleaching practice. Fuller's earth is found to be very effective in the removal of the excess yellow colors occurring in vegetable oils, but much less effective in the removal of the red colors usually accompanying them. To insure the removal of the red colors, large quantities of Fuller's earth must be used. Many of the vegetable decolorizing carbons are particularly good for the removal of the reds by the use of a combination of Fuller's earth and decolorizing carbon, each doing the work for which it is particularly fitted. The total amount of bleaching solids can be cut down considerably. This combination has now become standard practice with oils such as cotton seed, peanut and corn for food purposes, soya bean for industrial uses, and linseed oil for paint manufacture. A well-decolorized linseed oil allows the production of paints which retain their whiteness for much longer periods than those paints made with unbleached oil. Examples of this type of paint are found in the widely advertised "mill whites."

With oils like coconut, palm and palm kernel, where the yellow color is not so high as in the preceding group and it is chiefly the removal of the red color that is required by the refiner, industrial practice has shown that small percentages of vegetable carbons will do considerably better work alone than the high percentages of Fuller's earth previously used.

Vegetable carbons for oil decolorization are of the same type as the fine powders employed in the decolorization of aqueous liquids. Oil decolorizing carbons are ordinarily alkaline, — that is, their water extract will show pH values of nearly 7. Decidedly acid carbons are to be particularly avoided, for their use will increase the free fatty acid content of the oil undergoing refining. Excessively alkaline carbons are also to be avoided. They introduce the possibility of soap formation which may affect the filtration rate or cause darkening of the oil during deodorization.

Vegetable oil processing usually consists of three steps: First, the neutralization of free fatty acid by dilute solutions of caustic (at definite temperatures which are characteristic for each oil) and the removal of the soaps formed; second, bleaching of the oil; and third, deodorization. Vegetable carbons as such in the small quantities in which they are used have relatively small gathering power for the colloidally suspended soaps resulting in the refining. Quite often small amounts of Fuller's earth, Filter-Cel, diatomaceous earths are employed to aid in gathering the soaps. Stirring must be quite effective. Bleaching is usually more efficient and rapid at temperatures obtainable by steam heating than at ordinary room temperatures.

Vegetable carbons in oil decolorization, due to their high adsorbing properties, also effect considerable deodorization. Fuller's earth used alone on vegetable oils imparts to the oils a disagreeable earthy flavor which is particularly objectionable in a product intended for edible purposes. Even when only small amounts of a vegetable carbon are used in combination with Fuller's earth, the vegetable carbon will

entirely remove the odor or flavor imparted to the oil by the Fuller's earth.

With a bleached oil that is slightly rancid, treatment with vegetable carbons will often eliminate the necessity for more drastic treatment. Often with unbleached oils, both bleaching and removal of rancidity may be effected in one operation by the use of greater amounts of vegetable carbon than are required by a prime oil. The distinct deodorizing effect of vegetable carbons on oils is easily seen when it is noted that less steam is required in the deodorizing plant to deodorize effectively when carbons are used than when they are not employed.

It is often stated that there is considerably decreased loss due to oil retention when vegetable carbons are substituted for Fuller's earth. Carbons vary widely in their oil retention values which are functions of their apparent densities. The quantities of the carbon employed may run as low as one-twentieth of a per cent in the case of materials like lard; an eighth of one per cent with coconut oil where the decolorizing carbon is usually employed alone; 1 to 3% with cottonseed, peanut, soya bean and corn oils, being the weights of the total amount of bleach, the bleach composition being approximately 1 part of carbon to 12 parts of earth; 2 to 5% with linseed and rapeseed oil; and 1 to 3% with tallow and greases, the bleach composition being 1 part of carbon to 12 parts of earth. Because smaller amounts of carbon for the same effective color removal are used than Fuller's earth, the oil losses in the filter press cake are considerably less in the case of decolorizing carbons. In most cases the temperature treatment is from 160 to 180° F., except in the case of peanut and olive oils where the temperature is 120 to 140°. There are wide variations in bleaching temperatures in individual plant practices; some operators state that they obtain best results at 180 to 220°. A large number of plants expel moisture from the oil by heating before the bleaching mix is stirred in. The time of contact varies from 15 minutes to a half hour.

Considerable experimental work has shown a definite commercial adaptability of vegetable carbons to the de-colorization and deodorization of fish oils, such as cod, seal, whale, herring and menhaden, which are exceedingly difficult to refine under ordinary conditions.

For the sake of completion in this discussion, it is interesting to point out some of the results from the experimental data of a quantitative nature on the adsorption by charcoal of various ions. Osaka¹⁹ found that the adsorption with salts of the same base decreased in the following order: iodide, nitrate, bromide, chloride, and sulphate. The potassium salts are more strongly adsorbed than the corresponding sodium salts. Rona and Michaelis²⁰ find that the order of adsorption of the anions is hydroxide, sulpho-cyanide, iodide, nitrate, bromide, chloride, phosphate and sulphate; and of the cations, hydrogen, aluminum, copper, zinc, magnesium, calcium, ammonium, potassium and sodium. Schmidt²¹ in his study of the adsorption of acetic acid by charcoal finds the Freundlich equation does not quite represent the true situation. Many formulae for the adsorption of materials from aqueous solutions have been proposed, among them being those of Freundlich,²² McBain,²³ Schmidt,²⁴ and von Geogievics.²⁵ The exponents in adsorption isotherms when the Freundlich equation is used are given in the table.

As a name for the phenomenon observed when charcoal which has previously adsorbed a material gives up that material, the term "negative adsorption" has been applied. Osaka²⁶ found that sodium nitrate, potassium bromide, potassium iodide and potassium nitrate are adsorbed positively by blood charcoal, while sodium chloride, sodium

¹⁹ Mem. Coll. Sci. Kyoto Univ., vol. 1, p. 257 (1915).

²⁰ Biochem. Ztg., vol. 94, p. 240 (1919).

²¹ Zeit. Physik. Chem., vol. 77, p. 650 (1911).

²² Zeit. Physik. Chem., vol. 57, p. 385; vol. 59, p. 284 (1907).

²³ J. Chem. Soc., vol. 91, p. 1683 (1910).

²⁴ Zeit. Physik. Chem., vol. 74, p. 689 (1910).

²⁵ Zeit. Physik. Chem., vol. 83, p. 269 (1914).

²⁶ Mem. Coll. Sci. Kyoto Univ., vol. 1, p. 257 (1915).

sulphate and potassium sulphate are apparently adsorbed negatively. The solution of potassium chloride is adsorbed positively when the concentration is comparatively high, and is apparently adsorbed negatively when the concentration is comparatively low. With sodium sulphate the increase in concentration was about 1% and was less than that with the other salts. Walter²⁷ found that a number of materials in benzene and toluene show strong negative adsorption.

TABLE XXII
EXPONENTS IN ADSORPTION ISOTHERMS

<i>Solvent</i>	<i>Solute</i>	<i>Solid</i>	<i>n</i>	<i>Observer</i>
Alcohol	Iodine	Charcoal	4.0	Schmidt ¹
Benzene	Iodine	Charcoal	4.0	Schmidt
Water	Acetic acid	Charcoal	2.0	Schmidt
Water	Succinic acid	Charcoal	2.0	Schmidt
Water	Oxalic acid	Charcoal	10.0	Schmidt
Water	Potassium chloride	Charcoal	1.0	Lachs and Michaelis ²
Water	Milk sugar	Charcoal	4.5	Wagner ³
Water	Cane sugar	Charcoal	8.2	Wagner

¹ Zeit. Phys. Chem., vol. 15, p. 56 (1894).

² Zeit. Elektrochemie, vol. 17, p. 2 (1911).

³ Zeit. Kolloidchemie, vol. 8, p. 126 (1911).

The equilibrium represented by an adsorption isotherm is a reversible one and can be reached from both sides in a number of cases. While the adsorption equilibrium is theoretically a reversible one, there are conditions under which there may be apparent or actual irreversibility. If charcoal takes a dye out of solution to such an extent as to decolorize the water, no amount of washing with water will give a colored solution, even though dye is being taken out all the time.²⁸

Since adsorption is essentially specific, the amount of

²⁷ Koll. Ztg., vol. 14, p. 242.

²⁸ Freundlich and Neumann, Zeit. Physik. Chem., vol. 67, p. 538 (1900).

adsorption will necessarily vary with the nature of the adsorbing agent, the liquid and the substance to be adsorbed. Charcoal adsorbs benzoic acid about ten times as strongly as acetic. Charcoal adsorbs both acid and basic dyes while an adsorbent like alumina takes up many acid dyes readily and not the basic dyes; and silica and tannin adsorb the basic dyes more readily than the acid ones. Davis²⁹ found that the order of adsorption of iodine from different liquids was not the same with different forms of charcoal. With animal charcoal there was decreasing adsorption in the order chloroform, alcohol, ethyl acetate, benzene and toluene. With sugar charcoal, the order became chloroform, toluene, ethyl acetate, benzene and alcohol; whereas for coconut charcoal the order was toluene, chloroform, benzene, alcohol and ethyl acetate. Charcoal will decolorize aqueous solutions of iodine or of methyl violet, but alcohol will extract the color from the charcoal.

Graham and Hofmann³⁰ showed that strychnine, when introduced experimentally into beer, was completely removed by adsorption with charcoal. Skey³¹ reports that diluted sulphuric acid can be freed from traces of nitric acid by shaking with charcoal, while concentrated sulphuric acid cannot be.

Adsorption by chars of electronegative, electropositive and amphoteric substances were shown by Hauge and Willaman (L.C.) to be greatly affected by the reaction of the medium from which material was being adsorbed. On this basis an explanation is found for the results secured by different investigators on which exaggerated claims for the various commercial carbons showing 20, 30, etc., times the efficiency of its competitors were based. The differences have not been so much due to the properties of the carbons as to the reaction of the media.

The explanation of the influence of pH may be found in

²⁹ J. Chem. Soc., vol. 91, p. 1682 (1907).

³⁰ J. Chem. Soc., vol. 5, p. 713 (1853).

³¹ Chem. News., vol. 17, p. 217 (1886).

the electrical theory of adsorption and the effect of hydrogen and hydroxyl ions on the size of the charges on particles. Results show that in general the adsorption efficiency of carbons is dependent largely on the difference in electrical potential between the carbon and the adsorbate. The generalized curves are given in Fig. 55. In industry, the extreme ranges of pH necessary to most efficient adsorption of all types of compounds are often not permissible. Tanner³² states therefore the use of Fuller's earth, kaolin and other

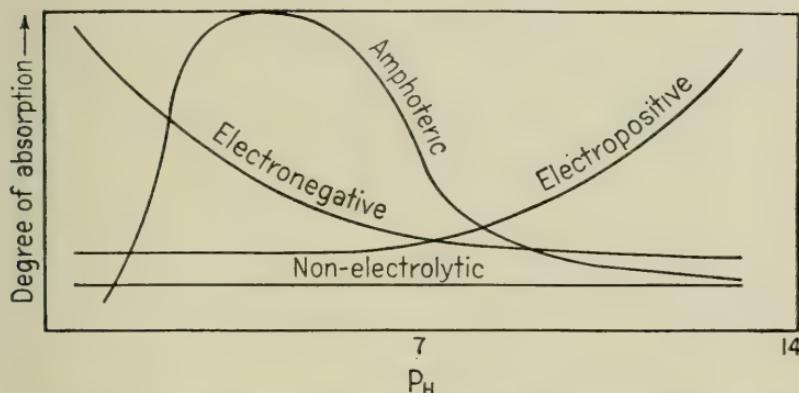


FIG. 55.—GENERALIZED CURVES SHOWING RELATION BETWEEN HYDROGEN ION CONCENTRATION AND ADSORPTION BY CHARS OF SUBSTANCES HAVING VARIOUS ELECTRICAL PROPERTIES

substances which possess electrical charges different from carbon, might under some conditions be more advantageously used (with greater efficiency) for the adsorption of certain substances.

The industrial value of carbon might be increased if a carbon were produced which would be active at the permissible pH for the substance to be adsorbed. The electrical properties of carbon can be greatly modified by activation (vide e.g. metal adsorbent chars). Owaga³³ has shown that the isoelectric point of carbon was shifted during the process

³² J. Ind. Eng. Chem., vol. 14, p. 441 (1922).

³³ Biochem. Ztg., vol. 161, p. 275 (1925).

of activation by heat alone. Perhaps future research will bring forth for decolorizing use a carbon which will be positively charged at all pH's. This would be an excellent addition to our present chars, since most colored impurities met in the industries are negatively charged.

CHAPTER XIX

METAL ADSORBENT CHARS

ALKALINE activated chars which can be used for removing metals such as gold and silver from their solutions, are structurally identical, according to McKee and Horton,¹ with ordinary decolorizing carbons and can easily be converted into them by acid treatment. This change is not mere neutralization, for the original properties cannot be restored by alkaline washing. A drastic treatment with alkali at about 850° C. is required. Like colloids, the alkaline char remains suspended in water, possesses a negative electric charge, and at a definite pH (3.8) flocculates and settles rapidly. At this pH it becomes electrically neutral, loses its metal adsorbing power, and becomes an ordinary decolorizing char.

The action of various chars under the influence of an electric field is interesting. The alkaline chars, when suspended in pure water, move toward the positive pole, whereas the acid-treated chars are practically stationary. This indicates that the alkaline chars are negatively charged and that the acid-treated chars are neutral or at their isoelectric point. A char made with soluble alkaline impregnating agents such as sodium carbonate and then thoroughly washed will be practically inert in a neutral or only slightly acid solution. If this char be previously treated with acid, washed, and even ignited to red heat, it behaves as a normal decolorizing char. This change in the nature of the char is fundamental and has nothing to do with the question of the reaction of the medium to be decolorized. In other words,

¹ Chem. & Met. Eng., vol. 32, pp. 13-16, pp. 56-59, 164-167 (1925).

the char has been conditioned to act in a specific manner. The original alkaline char is very effective as a metal absorbent, which property is practically lost on treatment with acid and is not regained by treating the char with an aqueous solution of an alkali.

Early in the 19th century, Graham,² Weppen,³ Lazowski,⁴ Percy,⁵ and Rose⁶ obtained metallic precipitates on charcoal from solutions. By the middle of the century a considerable amount of empirical knowledge had been published.

The first use of charcoal as a precipitant in metallurgy seems to have been made by W. N. Davis⁷ in connection with chlorination. Some of the older metallurgists, such as Eggleston writing in 1890 and Rose in 1896, discussed this topic. Later on, charcoal was used in a number of chlorination plants especially in Australia. Much information has been published on the use of charcoal as a precipitant in the chlorination process. Nardin⁸ describes its use at Mt. Morgan in Queensland, while Avery⁹ describes the reduction of gold chloride by charcoal, and Rose, in the 1915 edition of his *Metallurgy of Gold*, discusses charcoal as a gold precipitant.

As the cyanide process gradually replaced the chlorination process, it was natural that charcoal should be tried as a precipitant for the precious metals from cyanide solution. W. D. Johnson¹⁰ patented the use of charcoal in pulverized form for this application in 1894. Christy¹¹ discusses the commercial application of charcoal in cyanide practice. The use of charcoal as a precipitant in the cyanide process became

² Dingler Polytechn. Jour. Jahrg., 40, pp. 443-446 (1831).

³ Liebig Ann. Chem. Jahrg., 55, p. 241 (1845).

⁴ Chem. Gaz., vol. 6, p. 43 (1848).

⁵ Metallurgy — Part I, London, 1880.

⁶ Metallurgy of Gold, London, 1896, p. 277.

⁷ U. S. Patent 227,963 (1880).

⁸ Eng. and Mining Jour. (1901), p. 85.

⁹ Jour. Soc. Chem. Ind., vol. 28, p. 255 (1908).

¹⁰ U. S. Patent 522,260 (1894).

¹¹ Trans. A. I. M. E., vol. 26, p. 748 (1896).

general in Victoria,¹² although its use in the United States was confined almost entirely to a few isolated cases of precipitation from waste solutions. This application was discussed by A. W. Allen in the third edition of Julian and Smart's "Cyaniding Gold and Silver Ores."¹³ With the spread of knowledge concerning the adsorptive properties of charcoal in metallurgical practice, it was shortly determined that gold was precipitated more readily and in greater amounts than silver.¹⁴ Later it was learned that free cyanide had a deleterious effect, as shown by the work of Christy, Julian, Smart and Busey.¹⁵ The manner of using the charcoal was very inefficient. Undoubtedly the charcoal itself was not very active. As precipitation practice with zinc shavings and zinc dust improved and became better understood, the use of charcoal and interest in it gradually declined.

When the effect of carbonaceous matter in ores began to be discussed, interest in charcoal revived and caused the first definite experimental work. This was done by Morris Green¹⁶ in 1913, and was shortly followed by that of W. R. Feldtmann.¹⁷ The work of these two investigators materially advanced the knowledge of charcoal precipitation by submitting theories that were promptly controverted. A large number of theories were advanced to explain the facts. Konig¹⁸ assumed that the gold was reduced by chemical action. Green showed that any carbon dioxide evolved (which evolution was assumed by the older theories to be due to reduction of the gold salt with oxidation of the carbon) is simply due to displaced gas liberated by immersion in the solution. If the char be previously boiled with water to

¹² Power, Australian Min. Stand., 1897, p. 2305; Clark, *Ibid.*, 1901, p. 184; MacTear, *Trans. Inst. Min. & Met.*, vol. 6, p. 43 (1897-8); Gray, *Trans. Austral-Asian Inst. Mining Eng.*, vol. 5, p. 141 (1898).

¹³ *Cyaniding Gold and Silver Ores*, 3rd Edition, Phila., 1921.

¹⁴ Lowles, *Trans. Inst. Min. & Met.*, vol. 7, p. 190 (1898-9).

¹⁵ Busey, *Bull. Colorado School of Mines*, vol. 3, #2, Jan., 1906.

¹⁶ *Trans. Inst. Min. & Met.*, vol. 23, p. 65 (1913-14).

¹⁷ *Trans. Inst. Min. & Met.*, vol. 24, p. 329 (1914-15).

¹⁸ *Chem. News*, vol. 45, p. 215 (1882).

eliminate the adsorbed gases, no carbon dioxide is evolved although the gold is equally well precipitated. Many of the earlier theories assumed a reduction by some reducing gas in the charcoal, usually assumed to be carbon monoxide, although electrical action, osmotic pressure and catalysis were also suggested.

In 1915, A. W. Allen¹⁹ proposed research on the use of colloidal or finely divided carbon as a precipitant. In 1916 the announcement was made of the use of finely divided charcoal as a precipitant in place of zinc at the Yuanmi Mine, in Western Australia. Moore and Edmonds developed and put in practice a method of precipitation on charcoal. They quenched red hot charcoal, pulverized it very fine, and passed the solution from which the metal was to be adsorbed through three successive charcoal filters.²⁰ Their work gave a considerable impetus to the use of charcoal and the topic was widely discussed. It was still believed that carbon monoxide was in some way accountable for the action until A. W. Allen, in discussing Edmonds' paper,²¹ criticized the different theories. He definitely advanced the theory²² that the proper explanation was adsorption as aurocyanide. As all the known facts seemed to bear him out, Allen's conclusions were generally accepted. Recently Williams²³ published further data of experiments with laboratory solutions of a character entirely different from plant solutions, made at Yuanmi, showing that the sodium in the ash from the burned charcoal was far from sufficient to account for the simple adsorption of sodium aurocyanide. McKee and Horton²⁴ state that there is some evidence that metal adsorption by charcoal is a combination of both molecular and ionic processes, and that as the metal becomes more noble,

¹⁹ Trans. Inst. Min. & Met. (1915).

²⁰ Australian Patent 566, Feb. 2, 1917; U. S. Patent 1,368,520 (1921).

²¹ Trans. Inst. Min. & Met., vol. 27, pp. 277-316 (1917-18).

²² Chem. & Met. Eng., vol. 18, p. 642 (1918).

²³ Mining Mag., London, vol. 28, p. 139, 1923.

²⁴ Chem. & Met. Eng., vol. 32, p. 164 (1925).

the ionic or hydrolytic factor becomes the more dominant in adsorption. For various reasons, they expect that gold would be precipitated chiefly as metal from aurocyanide solutions except at the beginning of adsorption when a certain amount of compound would be taken up. Gross and Scott²⁵ confirm the results of Williams insofar as laboratory solutions of cyanide are concerned. They find with such solutions that the mechanism of the precipitation of gold from cyanide solutions by charcoal involves adsorption accompanied by a chemical change, thereby completely reversing the opinion expressed by them in a paper read before the American Institute of Mining and Metallurgical Engineers at San Francisco in January, 1923. They confirm observations previously made that the precipitation of silver on charcoal is slower because charcoal has less capacity for silver than for gold. They observe, however, that silver precipitation follows the same laws as gold precipitation. They find, as did McKee and Horton, that the limit of charcoal precipitation from cyanide seems to be about 2,000 ounces of gold and about 1,000 ounces of silver per ton of charcoal.

Gross and Scott, as a result of extended experiments find that little difference exists among charcoals prepared from different woods. The metal adsorbent chars are the soft charcoals resulting from vegetable materials charred at low temperatures. Cokes, coals and hard natural chars are poor metal adsorbers. When capacities, or loads of metal, charcoal is able to take, are compared, the harder woods in general are less efficient than the softer woods, although the differences are not large. There is relatively little difference in the activity of charcoals made from different woods. The activity is a measure of the rate at which charcoal, irrespective of its ultimate capacity, adsorbs gold or silver. It is measured by the percentage of metal (of the solution) precipitated, while the capacity is measured in ounces of metal per ton of original weight of charcoal. Gross and Scott find that preliminary treatment of the wood with materials such

²⁵ Technical Paper #378, Bureau of Mines, 1927.

as potassium cyanide, sodium sulphide, nitric acid, zinc chloride, calcium hydroxide, sodium hydroxide, selenium oxychloride as activating agents does not give promising results and that hydroxides are actually detrimental. This does not seem to agree with the work of McKee and Horton, who find that water soluble alkaline impregnating agents cause the carbons to have metal adsorbent properties. Gross and Scott find that the most important detail in charcoal activation is heat treatment accompanied by oxidation with either steam or air. This is in accordance with the theories of Chaney, discussed under gas adsorbent carbons. Quenching does not seem to increase the efficiency of the charcoal. McKee and Horton state that "Treatment with sodium carbonate at about 900° C, followed by hot quenching in water, gives products much superior to any hitherto used in commercial cyanide practice."

The apparent activation of the charcoal by quenching may be traced to heating before quenching, although quenching in chemical solutions such as nitric acid, zinc chloride and sodium hydroxide increased the activation of the charcoal. From their experiments, Gross and Scott conclude that zinc chloride, nitric acid and selenium oxychloride treatments after charring of the charcoal seem to give promise of increasing the efficiency, whereas potassium cyanide, sodium sulphide, sodium hydroxide, calcium hydroxide and sulphuric acid decrease the efficiency, although subsequent heating and quenching restore the original efficiency. In use, grinding of the charcoal finer than 200 mesh is of little benefit and excessively fine grinding is detrimental.

Investigation showed that charcoal does not change in weight after wetting and drying at 60° C., so that the dry weight, whether the charcoal be crushed wet or dry, represents the same amount of charcoal at all times. For all their work, Gross and Scott employed a standard charcoal made of pine wood charred in covered crucibles at 900° C. for a half hour after the inflammable gases ceased coming off. The material was then cooled in the covered crucibles, pulverized

to pass a 200-mesh sieve and weighed dry after drying for several hours at 60° C. They found that charcoals from different materials gave different results. Different results were obtained from the same charcoal made at varying temperatures with varying times of carbonization and quantities of air. Different results were obtained within a limited range with different finenesses of the same material, with different ratios of charcoal to the solution, or with varying gold and silver contents of the solutions, as well as differences in times of contact between the charcoal and the solution. Temperature in some cases was quite important.

There is considerable evidence in favor of the theory of adsorption accompanied by chemical reaction. When gold and silver particularly are adsorbed by charcoal from cyanide solutions, the adsorbed material is not visible as a metallic precipitate, while the metal adsorbed from a chloride solution in the case of gold and from a nitrate solution in the case of silver, is visible. Brussow²⁶ has shown that gold precipitated on charcoal from a chloride solution is soluble in aqua regia, bromine and chlorine water, and that gold deposited from a cyanide solution is stated by Feldtmann²⁷ not to be thus soluble. Feldtmann,²⁸ Edmands,²⁹ and Williams³⁰ have shown that sodium sulphide, potassium hydroxide and a cyanide solution are "solvents" for the metals "precipitated" on charcoal from cyanide solutions. Sodium sulphide has a high dissolving power for gold deposited on charcoal from cyanide solutions, but a low "dissolving" power for metallic gold precipitated from chloride solutions. Sodium sulphide has no effect whatever in "dissolving" silver from charcoal, whether precipitated from cyanide or nitrate solution. It is usually thought that when the visible metallic precipitate on charcoal is dissolved by a cyanide solution

²⁶ Ztschr. Chem. u. Ind. Koll., 1909, p. 137.

²⁷ Trans. Inst. Min. & Met., vol. 24, p. 329 (1914-15).

²⁸ Ibid., vol. 24, p. 329 (1914-15).

²⁹ Ibid., vol. 27, p. 277 (1917-18).

³⁰ Mining Mag., vol. 28, p. 139 (1923).

and subsequently deposited in an invisible form, a different precipitate has been formed. A. W. Allen, who advanced the adsorption theory, has endeavored to convince, in several published statements, that this is not a normal instance of simple chemical solution but rather an example of disturbance of adsorption equilibrium and the release of the adsorbed compound. Gross and Scott have shown, in studies on charcoal loaded with gold from a chloride solution to approximately 1,050 ounces per ton, and another charcoal loaded with silver from a nitrate solution to approximately 650 ounces per ton and then treated with cyanide solutions, that the adsorption of the new precipitate follows the dissolution of the metallic precipitate so rapidly that part of the change is practically instantaneous and that some of the dissolved metal never gets outside of the pores of the charcoal.

Many observers have stated that there is an apparent saturation point to the capacity of the charcoal for metals deposited from cyanide solution. There seems to be no similar limit for metallic precipitation. In Bureau of Mines tests loads of 16,700 ounces of gold per ton were obtained from a chloride solution, and a load of 3,700 ounces of silver per ton from a nitrate solution. Both metals were plainly visible as metallic precipitates. From cyanide solutions, however, the load limit on pine charcoal was about 2,000 ounces of gold per ton and 1,000 ounces of silver per ton.

A summary of the results of most of the workers in the field of metal adsorbent carbons shows that adsorption is very rapid and approaches an equilibrium in any given solution. The temperature effect is small. As in the case of decolorizing carbons, metal adsorbent chars take out a greater proportion of the material adsorbed in the case of weak solutions than from strong ones, although greater amounts may be adsorbed from the stronger solutions. Most workers agree that there is a maximum adsorption which does not increase beyond certain increased concentrations of solutions. As in the case of other adsorbent carbons, the phenomenon seems to follow the exponential equation. Ad-

sorption and the rapidity with which equilibrium is reached depend upon the kind and condition of the adsorbent. Adsorption seems to be proportional to the equivalent or atomic weight of the adsorbed substance. Acids greatly increase the absorption of anions of neutral salts. From a mixture of substances in solution less of either substance is adsorbed than from a solution of one of the substances. Although it is assumed to be true that adsorption is proportional to surface, there is still lacking definite experimental evidence to this effect, inasmuch as increased fineness of grinding does not materially increase the already enormous surface of the charcoal.

It was thought that simple adsorption of the gold or silver salt took place without chemical change when charcoal adsorbed these metals from solution. There are two reasons for this belief. The color reaction obtained on heating a loaded gold charcoal has been noted by Reid³¹ to pass through the same identical range of colors as an alkaline aurocyanide. When such a solution is heated gradually, it passes through a range of colors, first pink, then red, then a deep brownish or purplish red, and finally metallic gold. Aurous cyanide, on the contrary, becomes green when heated, then changes to brown and finally to metallic gold. Secondly, when hot water extracts are made from a gold loaded charcoal, after evaporation and heating they pass through the same range of colors under the same conditions as does the alkaline aurocyanide. Investigation showed, however, that the solution after adsorption consisted almost entirely of a bicarbonate and that the alkali metal from the alkaline gold or silver cyanide remained in solution. Williams³² states that the sodium necessary for the simple adsorption of $\text{NaAu}(\text{CN})^2$ was not found in the charcoal ash. Gross and Scott therefore conclude that a chemical action accompanies the adsorption. McKee and Horton have pointed out that as a metal becomes more noble, ionic adsorption may become the

³¹ Chem. Eng. & Min. Rev., vol. 10, p. 374 (1918).

³² loc. cit.

more dominant factor. What may actually happen in the adsorption from cyanide solution is that the aurocyanide ion or argentocyanide ion is adsorbed as such. If this be assumed to happen, the assumption that chemical action accompanies the adsorption, and that if calcium be available in the charcoal a double salt, apparently calcium aurocyanide, is adsorbed, becomes unnecessary. Calcium is always available in large quantities in a working solution. Most of the cyanide used in practice is probably calcium cyanide. With certain types of alkaline activated chars it can be shown that copper ions may be adsorbed from copper sulphate with increase of the sulphuric acid content of the solution. This is shown very well in Fig. 56, in which the change of copper adsorption has been plotted against original concentrations of solutions, and the pH values of original solutions and of filtrates are also plotted. At low concentrations the adsorp-

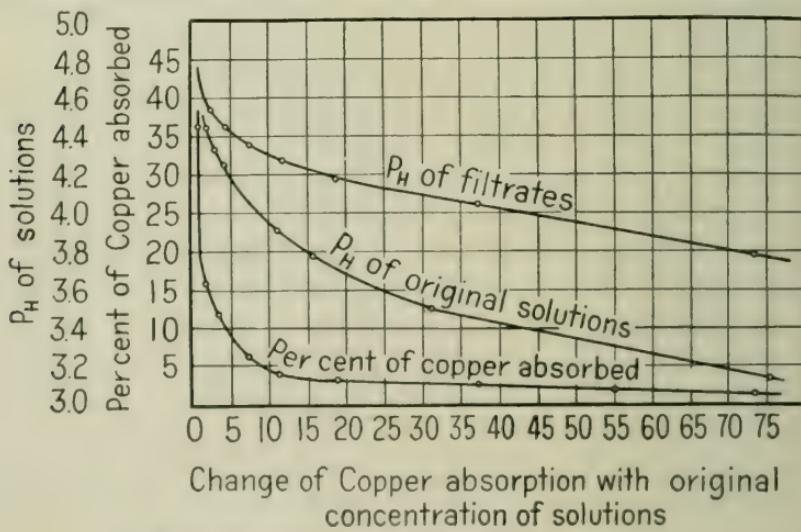


FIG. 56.—METAL ABSORPTION BY CARBON
(McKee and Horton)

tion may be assumed to be ionic, although at higher concentrations there is no doubt that some of the metal is adsorbed in the form of a complex ion or molecule.

Chaney shows that the adsorption of gold from a solution of a simple salt is proportional to the retentivity of the carbon or its activity as defined in percentage of iodine removed from a solution in a standard test. These terms and their

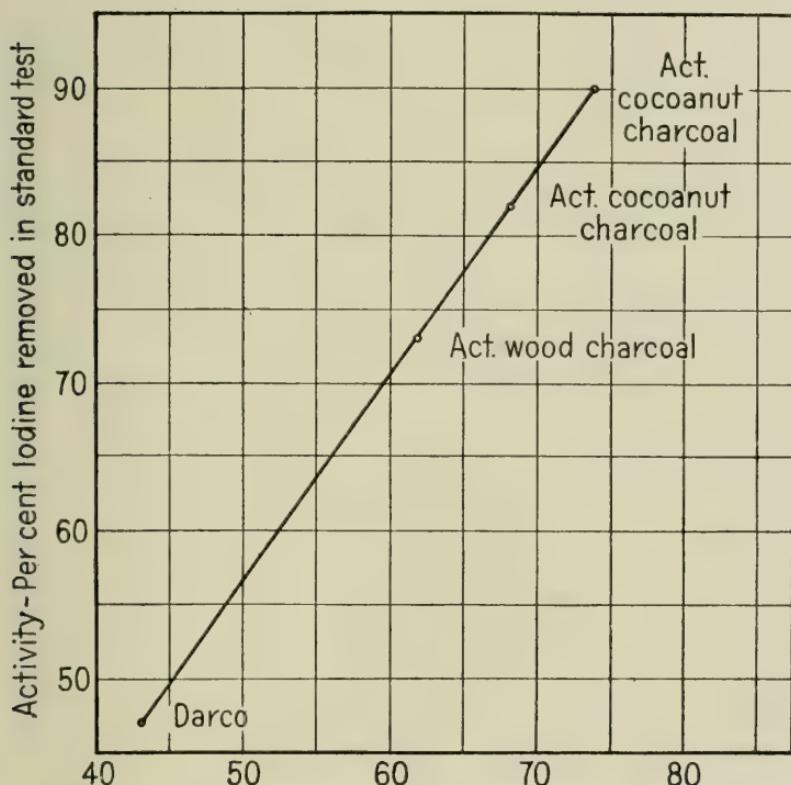


FIG. 57.—REMOVAL OF GOLD FROM GOLD CHLORIDE SOLUTION BY ACTIVATED CARBON OF DIFFERENT ACTIVITIES

All carbons pulverized to pass 200 mesh, acid extracted, thoroughly washed, and dried before testing. Equal weights of carbons agitated with gold chloride solution at 25° C. for 10 minutes. (Chaney)

applications were discussed under gas adsorbent carbons. Fig. 57 shows that the removal of gold from a solution is proportional to the activity of the carbon.

When activated industrial carbons are employed for adsorption of gold and silver values from cyanide solutions, it

INDUSTRIAL CARBON

is found that many of them are superior to wood charcoals. Table XXIII gives the results of activity and capacity for some gas-adsorbent charcoals and decolorizing carbons. The material termed "Burrell 40-minute" is an adsorbent carbon used for gasoline extraction from natural gas. Those termed "Barnebey-Cheney" carbon are bright, hard, dense granular carbons, finer than 60 mesh and usually considered

TABLE XXIII
INDUSTRIAL CHARCOALS AS METAL ADSORBENTS
(from Gross and Scott)

Charcoal	Activity		Capacity	
	Precipi- tation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
Pine.....	48.7	100.0	1,363	100.0
Burrell 40-minute ¹	3.1	6.4	814	59.7
Do. ²	57.0	117.0	1,317	96.6
Do. ³	99.3	203.9	1,715	125.8
Barnebey C.145A ¹	28.6	58.7	579	42.5
Do. ²	48.1	98.8	1,126	82.6
Do. ³	99.1	203.5	2,080	152.6
Barnebey C.156A ¹	29.8	61.2	774	56.8
Do. ²	37.1	76.2	955	70.1
Do. ³	88.4	181.5	1,722	126.3
70-minute Absorbite ¹	10.4	21.3	840	61.6
Do. ²	62.5	128.3	1,348	98.9
Do. ³	96.1	197.3	1,559	114.4
Super-Filtchar ¹	21.0	43.1	1,226	90.0
Do. ²	61.1	125.5	1,356	99.5
Do. ³	82.3	169.0	1,646	120.8
Suchar ⁴	59.0	121.1	644	47.3
Do. ⁵	82.3	169.0	1,053	77.3
Kelpchar ¹	15.3	31.4	261	19.2
Do. ⁵	39.5	81.1	853	62.6

¹ = Coarse portion only, over 16 mesh, not pulverized.

² = Pulverized dry to pass 200 mesh sieve.

³ = Quenched and pulverized wet to pass 200 mesh sieve.

⁴ = As received.

⁵ = Quenched only; not pulverized further.

of the gas adsorbent type. Super-Filtchar and Suchar are of the decolorizing carbon type made from black ash residues. Kelpchar is a light, rather fine material produced by the carbonization of kelp. Absorbite is a commercial gas-adsorbent char made from coconut shells. When the coarse material is filtered from these carbons and employed separately, it is found that they are poorer metal adsorbents than the same material pulverized to pass a 200 mesh sieve.

When the same carbon is employed in tests, it is found that few substances in solution have a bad effect on the precipitation of gold and silver by charcoal. This is shown in Table XXIV. In the tests, pine charcoal was used in solutions containing one pound of free cyanide and one pound of the additional substance per ton. The substances that are most effective in lowering the capacity of the charcoal for precipitation are generally also good solvents for the adsorbed material. This is a natural result since it is known that the solvent power counteracts precipitation. As a result of other tests, it has been found that sodium sulphide in solution decreases the precipitation of gold. Free cyanide in solution decreases the precipitation of both gold and silver. Hydroxides in solution, when present in amounts less than half a pound per ton, increase the precipitation of both gold and silver, but when present in greater amounts decrease it.

In commercial work there are only a few methods applicable to the recovery of the adsorbed metal from the charcoal. Amalgamation, as would be expected, is of no value. Sodium sulphide in solution will remove virtually all the gold from a loaded charcoal. It is of little value, however, on adsorbed silver. As a rule, a substance that dissolves the adsorbed gold also dissolves the corresponding silver material, the outstanding exceptions being sodium sulphide which dissolves only the gold, and mercurous nitrate which dissolves only the silver. Hot cyanide solutions are effective solvents in both low and medium concentrations. Electrolytic recovery does not work. Attempts to operate

it have shown that the salt must be dissolved in the electrolyte before it can be deposited on the cathode.

Charcoal when employed in connection with cyanide solutions also adsorbs cyanide, the loss of which may become an important factor in commercial operation.

TABLE XXIV
EFFECT OF VARIOUS SUBSTANCES IN SOLUTION.
(from Gross and Scott)

Agent added	Activity		Capacity	
	Precipi- tation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
Potassium arsenate.....	71.1	113.2	1,321	118.4
Potassium ferricyanide.....	95.1	151.4	1,174	105.2
Sodium persulphate.....	98.2	156.4	1,171	104.9
Zinc chloride.....	87.1	138.7	1,142	102.3
Copper sulphate.....	65.5	104.3	1,117	100.1
None, average of 3 tests.....	62.8	100.0	1,116	100.0
Ammonium chloride.....	75.7	120.6	1,091	97.8
Ammonium carbonate.....	60.3	96.0	1,065	95.4
Ammonium hydroxide.....	50.8	80.9	1,013	90.8
Potassium nitrite.....	52.1	83.0	1,000	89.6
Potassium nitrate.....	51.2	81.5	992	88.9
Potassium chloride.....	47.9	76.3	989	88.6
Sodium chloride.....	45.9	71.7	987	88.5
Potassium ferrocyanide.....	49.4	78.7	986	88.4
Potassium cyanate.....	48.4	77.1	980	87.8
Sodium sulphate.....	46.6	74.2	978	87.6
Potassium sulphocyanate.....	47.3	75.3	968	86.7
Suspended clay.....	51.2	81.5	958	85.8
Sodium carbonate.....	42.3	67.4	958	85.8
Sodium silicate.....	50.3	80.1	946	84.8
Cupric chloride.....	51.3	81.7	935	83.8
Potassium carbonate.....	44.3	70.5	935	83.8
Sodium peroxide.....	41.6	66.2	922	82.6
Potassium zincate.....	38.0	60.5	821	73.6
Bleach powder.....	52.3	83.3	700	62.7
Tannic acid.....	29.9	47.6	677	60.7
Iodine.....	88.8	141.4	411	36.8

A large amount of work has been done to determine if it be possible to so treat the charcoal, after it has adsorbed a quantity of gold or silver, as to cause a change of the adsorbed substance and leave the charcoal free to take on another load. Reheating a loaded charcoal does not restore its adsorptive power. Various acids such as hydrochloric, nitric or hydrogen sulphide are not effective as fixing agents.

About the only practical method as yet available for the recovery of the metal which a charcoal has adsorbed depends upon destruction of the charcoal by combustion. The objections to charcoal as a precipitant are that large bulk and weight are required, especially for silver. There is a loss of cyanide due to its adsorption by the charcoal. At times the burning of the charcoal for a clean-up may be disadvantageous. On the other hand, charcoal has a large number of advantages.

The technical problems involved in the adaptation of charcoal for the removal of gold and silver from cyanide liquors appear to have been met successfully in hydrometallurgical plants in Australia. The use of lump charcoal is not feasible because of the low efficiency and bulk of the material to be smelted. The latest practice involves wet grinding of the char and forming a cake of the ground material on the leaves of a leaf filter. The liquor to be treated is passed through several units in succession, the strongest liquors meeting the partly loaded char and the weakest liquors the fresh char. The cakes are dropped at intervals and reformed, bringing new surfaces into action and materially increasing the capacity of the char. After washing and drying the cakes are burned to remove the carbon and the ash is collected and smelted with a special flux.

Charcoal is a clean precipitant and does not contaminate the solution with harmful substances. Fouling with zinc compounds is avoided. It is now well known that charcoal precipitates copper from cyanide solutions. Charcoal could be used to keep mill solutions free of copper. When charcoal is used, very few fouling agents affect the precipitation seriously.

Charcoal is comparatively cheap and is easily prepared. Practically all woods are satisfactory. The reader is referred to the chapter on charcoal as a fuel for methods of preparation, yields and the type of charcoal from various woods. Carbonization conditions may be easily controlled by regulation of the oxidation to give fairly well activated materials. This has been discussed under gas adsorbent chars. In use pulverization is necessary, but not to such a degree of fineness as to interfere with rapid filtration.

Charcoal for precipitating gold is readily and advantageously adapted to a small isolated plant. Fairly coarse charcoal employed in gravity filtration could be used cheaply. Countercurrent methods of treatment and treatment of low cyanide content solutions would prevent high cyanide losses. The charcoal could be burned and the ash melted to bullion at the plant. This would have to be done carefully to avoid dust loss.

Whether charcoal will replace zinc will depend on local conditions. Where a foul liquor is being treated, char will be cheaper than zinc under most circumstances, since the bullion is more easily refined and is valued at two to three dollars per ounce higher than that produced with zinc. This is especially true with liquors running high with antimony and arsenic. In isolated localities where wood is plentiful, it is estimated that the char process could displace zinc at about one half the cost. Pengilly,³³ von Bernewitz,³⁴ Julian and Smart³⁵ have shown in commercial practice that charcoal is an excellent precipitant for small amounts of gold or silver from waste solutions containing little or no free cyanide. In this case, cheap, simple operations with efficient precipitation can outweigh the increased load capacity of better charcoals. Filtration through beds of charcoal in stage precipitation necessitates only periodic addition of fresh char-

³³ Proc. Chem. & Met. Soc., So. Africa, vol. 2, p. 181 and pp. 234-236 (1897-99).

³⁴ Min. & Sci. Press, vol. 99, p. 758 (1909).

³⁵ Cyaniding Gold and Silver Ores, 3rd Edition, Phila., 1921.

coal and the removal of saturated material at the head of the filter. Low cyanide concentration or the absence of free cyanide would be beneficial.

When cyanide solutions are regenerated by acidification, charcoal may be advantageous. All the silver is readily precipitated, but owing to the slow formation of the aurous cyanide, only a part of the gold is thrown down. After filtration of the precipitate and removal of the hydrocyanic acid, the neutral or slightly acid solution is free from cyanide. The gold is in ideal condition for charcoal precipitation.

Gold and silver may be precipitated by adding pulverized charcoal, agitating, and recovering the charcoal by flotation in the case of cyanide ore pulps still containing precious metals in soluble form going to waste. The metal values may be recovered without the necessity of filtration of the pulp.

With research on activation at a standstill, the serious disadvantage in the use of charcoal for precious metal precipitation, especially silver, lies in the large volume of charcoal required. Gross and Scott calculated that "A mill treating 100 tons of ore a month, containing \$10 of recoverable gold per ton, would require about a ton of charcoal per month if the charcoal were loaded to 1,500 ounces per ton. A ton of pine charcoal pulverized to 50 mesh would occupy when wet about 90 cu. ft. A mill treating 100 tons containing 10 ounces of recoverable silver per ton would require 40 tons of charcoal per month, if the char were loaded to 750 ounces of silver per ton. This would necessitate burning over 100 cu. ft. of charcoal daily."

If charcoal is to have broad application in cyanidation, it will be very desirable to increase its adsorbing capacity for metals. It seems possible, however, that methods may be developed which will allow the fixing of the adsorbed material on the charcoal and allow it to take up a fresh load. This would be equivalent to increasing its capacity. There is still a large unexplored field of methods of activating charcoal to make it a more efficient agent.

To sum up, the factors favoring the use of charcoal are its advantages in the more complete removal of gold from foul liquors with the production of a higher grade of bullion and lower refining cost; the elimination of the introduction of fouling agents into the solution; and a lower cyanide consumption in ore treatment. In general, advantages to be gained by the use of char are such that when more efficient chars become available, the industry will undoubtedly take more interest in this very promising new development.

According to Skey,³⁶ antimony and arsenic can be removed so completely from solutions of their oxides or chlorides in moderately strong hydrochloric acid (with a little tartaric acid in the case of antimony) by charcoal that neither of them can be detected in the solution by the very delicate Reinsch or Marsh test, although before the treatment with charcoal they could be detected without difficulty. Commercial sulphuric and hydrochloric acids, diluted somewhat with water, can be purified of arsenic and antimony by agitating them intermittently for a short time with fresh charcoal and then filtering. The result is expedited by the application of heat. Lockemann and Paucke³⁷ have made a quantitative study of the adsorption of arsenic acid by charcoal. Animal charcoal also adsorbs small amounts of arsenic from aqueous solutions. Chapin³⁸ states that blood charcoal is effective as a purifying agent for arsenic solutions.

Other than in its specific applications to gold and silver metallurgy, the adsorbing power of chars for metals has been little studied. The adaptability of its application in removing metal contaminations opens up many interesting possibilities in many diverse applications in industry.

³⁶ Chem. News, vol. 17, p. 157 (1868); and vol. 36, p. 6 (1877).

³⁷ Ztschr. Koll. Chem., vol. 8, p. 273 (1911).

³⁸ J. Ind. & Eng. Chem., vol. 6, pp. 1002-3 (1914).

CHAPTER XX

PHARMACEUTICAL CHARCOAL

THE use of charcoal in medicine and pharmacy has grown rapidly in recent years. Many of the commercial synthetic vegetable carbons find application, in small tonnages to be sure, in the manufacture of various types of pills, digestive tablets and the like. The adsorbent action of charcoal for alkaloids, pathogenic bacteria, enzymes, toxins and poisons of various sorts is well known.

Rosenthaler and Türk¹ studied the action of charcoals of various types on codine, caffein, salicin, picrotoxin, gallic, tannic and oxalic acids. They found that these materials were adsorbed by the charcoal at ordinary temperatures, but that in many cases the charcoal exercised a powerful oxidizing action. In his experiments on the adsorption of resorcin, hydroquinol, acetanilide and cholesterol, Rosenthaler concludes that the ratio of adsorption is in proportion to the molecular weight of the material adsorbed. Hence it is not advisable to attempt to decolorize a substance with charcoal when the molecular weight of the substance is greater than that of the color present. Gordin and Kaplan,² in their study of the adsorption of alkaloids, glucosides, bitter principles and coloring matters of pharmaceutical materials, find that the complete removal of alkaloids necessitates digestion with continuous shaking of the charcoal in the solution for several hours. The removal of the alkaloids by charcoal is not influenced by the presence of free acid in the solution. Even alkaloids which in the free condition are water soluble, such as colchicine and caffein, can be com-

¹ Arch. Pharm., vol. 244, pp. 517-36.

² J. Amer. Pharm. Assoc., vol. 3, pp. 627-30.

pletely adsorbed by charcoal. Laqueur and Sluyters³ find that a number of commercial vegetable carbons are superior adsorbents for oxalic acid, potassium oxalate, mercuric chloride, strychnine nitrate, morphine sulphate and methylene blue, all of which are considered as poisons. Joachimoglu⁴ finds that there is a fair degree of parallelism shown between the adsorptive ability of a number of commercial carbons with a detoxicating power of the carbon in respect to strychnine nitrate. Approximately one-tenth of a gram of charcoal will detoxicate about one-hundredth of a gram of strychnine nitrate.

In the comprehensive use of charcoal in cases of infection, it is perhaps of greatest importance from a medicinal viewpoint to note that it is able not only to take up toxins and bacteria but also to counteract the acidity of intestinal contents arising through bacterial influence, action and evil consequences. Wiechowski⁵ finds that charcoal adsorbs crystalloids, colloids, bacteria, etc., so as to prevent their adsorption in the intestines of the body, but that its action is not extended to the blood. Wischo⁶ states that the more voluminous a charcoal is, the greater is its power of adsorbing toxins and bacteria. Blood charcoal, particularly after being shaken with blood serums, mucilage, pepsin or carbohydrates, is not saturated but still retains its power of decolorizing methylene blue solutions. He reasons, therefore, that the activity of the charcoal will not be affected when administered internally. Friedrich⁷ states that a cheaper substitute for blood charcoal which is required for fighting cholera and dysentery is necessary. These substitutes now exist in our synthetic vegetable carbons. Salus⁸ states that when water, contaminated by micro-organisms, is shaken

³ Biochem. Ztg., vol. 156, pp. 303-22 (1925).

⁴ Biochem. Ztg., vol. 134, pp. 493-9 (1923).

⁵ Kongr. inn. Med., Wiesbaden, 1914.

⁶ Pharm. Post. vol. 48, pp. 73-4 (1915).

⁷ Oesterr. Chem. Ztg., vol. 18, pp. 137-8 (1915).

⁸ Wien. Klin. Wochschrift, vol. 29, pp. 846-9; Chem. Zentr., 1916, II, 674-5.

with charcoal and filtered through paper, the clear filtrate is generally bacteria free, as the micro-organisms have been adsorbed by the charcoal. Charcoal, however, cannot be used for removing bacteria from milk, blood serum or other colloids, as the colloids are adsorbed more than the bacteria. Adsorption of bacteria by charcoal is selective. Coccii are adsorbed more than typhoid bacteria and the latter more than *bacillus coli*. Incarbon⁹ is a suspension of highly active sterile blood charcoal for intravenous use. Experiments with test animals have shown that it will form stable compounds with toxic doses of diphtheria and tetanus toxins when the latter are injected into the blood stream. It is stated to be without influence on the antitoxins normally developed in the animal.

Dingemause and Laqueur¹⁰ find that in their study of the distribution of mercuric chloride and strychnine nitrate between the pig's stomach and intestine and various types of charcoal, nearly one half of the mercuric chloride is adsorbed from the stomach while practically all is adsorbed from the intestine by the charcoal, and a similar adsorption of strychnine occurs. Eisler¹¹ notes the interesting fact that when charcoal adsorbs cholesterol its ability to adsorb saponin is greater than that of untreated charcoal under similar conditions, and its detoxicating power is accordingly enhanced. Likewise, charcoal loaded with saponin adsorbs somewhat more cholesterol than otherwise. The disinfecting power of phenol and mercuric chloride as regards cholera vibrios and typhus bacilli is more or less reduced by the presence of charcoal, the degree of effectiveness depending upon the adsorbability of these substances. Phenol is only partially adsorbed and its disinfecting action is little reduced, whereas mercuric chloride may be almost completely adsorbed with resultant greatly diminished toxicity. When either phenol or mercuric chloride adsorbed on charcoal is employed for

⁹ Chem. Zentr. 1918, I, p. 367.

¹⁰ Biochem. Ztg., vol. 169, pp. 235-44 (1926).

¹¹ Biochem. Ztg., vol. 172, pp. 154-70 (1926).

the disinfection of cholera or typhus bacilli, about 100 times as much disinfectant is required as when it is used in the free state. Houssay¹² found that the hemolytic substances of snake venoms are adsorbed by charcoal while antitoxic serum is not adsorbed. After adsorption with charcoal there remains in the venom a substance which can combine with antitoxin but which is not hemolytic. The remaining substance and that which combines with the charcoal, neither of which alone has any hemolytic action, are the two constituents of hemolysin. Charcoal thus is an effective detoxicating agent against snake venom.

Kolthoff¹³ studied the action of charcoals from the medicinal viewpoint, particularly as to their adsorption of the digestive enzymes. Hedin¹⁴ found that charcoal neutralizes trypsin in a manner similar to that effected by the tryptic anti-body found in serum. This process of neutralization can be divided into two stages. At first the trypsin is adsorbed directly by the charcoal and its complete adsorption can be easily effected by using a sufficient amount of charcoal. The trypsin merely adsorbed is readily transferred to added casein. Secondly, the trypsin is fixed in the charcoal and rendered inaccessible for added casein. The amount of trypsin fixed is larger the greater the amount of charcoal, the longer the time of interaction, and the higher the temperature. The action of charcoal has been found to agree with that of the tryptic anti-body in all respects. Falk and Sticker¹⁵ extended the work of Hedin. They found that charcoal strongly adsorbed trypsin and after adsorption the trypsin was without effect in splitting casein. Trypsin extracts passed through plant charcoal had the power to digest peptones, and tyrosine crystals were obtained. Falk and Sticker have tabulated the results showing the action of trypsin solutions which had been passed through charcoal

¹² Rev. Instituto Bact., vol. 2, pp. 197-230 (1921).

¹³ Pharm. Weekblad., vol. 56, pp. 207-25, 237-58 (1919).

¹⁴ Bioch. J., vol. 1, pp. 484-496.

¹⁵ Münsch. Med. Wochschr., vol. 57, p. 47.

on cattle serum, the blood serum of a person suffering from carcinoma, and the blood serum of a tuberculous cachexia patient. Wood charcoal lowers the anti-trypsic power of the serum. Plant charcoal has a power of adsorbing ferments and, in certain cases, anti-ferments to a limited extent. Especially prepared sterile charcoals were used in experiments with dogs suffering from carcinoma. Beneficial action as compared with plain trypsin injections was noted.

It is very likely that adsorbent carbon has wide possibilities in the field of medicine and that its application will be more varied when further work is done.

CHAPTER XXI

ELECTRODES

DEVELOPMENT OF THE CARBON ELECTRODE INDUSTRY

IN writing the biography of a living man, one of the first things to be mentioned is his age, for that gives an idea of the times in which he has lived and the experiences he has passed through. This, in a general way, is also true of an industry, for its age at least hints at the state of perfection to which it has been brought. To say that the manufacture of carbon electrodes on a commercial scale is but half a century old is therefore equivalent to calling attention to its phenomenal development.

The essential rôle of the carbon electrode in industry and in modern life has recently been pointed out by Hinckley,¹ who has shown carbon electrodes enter into the manufacture of the following materials:

Electric steel, ferro-alloys, calcium carbide, silicon carbide and related abrasives; aluminum, calcium and magnesium metals; phosphorus and phosphoric acid; electrical resistance wire; titanium and zirconium; carbon disulphide; tungsten; fixed nitrogen (cyanamide); sodium; caustic soda and chlorine; and all of the electric furnace alloys. The electrode today is therefore an essential part of our modern existence.

It shall be the purpose here to review briefly the technical history of this development, but before attempting this review it is perhaps desirable to direct attention to a condition which is peculiar to the carbon industries. While most

¹ A. T. Hinckley, "The Development of the Modern Furnace Electrode," Electrical World, vol. 78, No. 26, pp. 1263-5; December 24, 1921.

industries have a more or less abundant literature, with numerous books, pamphlets and articles, the manufacture of carbon electrodes is a notable exception. Were it not to be considered sarcasm, the industry might even be referred to as a "black art," first because of the secrecy usually surrounding its processes, and second, because of the absolute physical dirtiness of the usual electrode plant. Carbon works have generally been regarded as fortifications, through whose gates only the initiated might enter. Most of the manufacturers have been of the opinion that the less said on the subject the better for them. One reason for this, perhaps, is that in Europe, the art of manufacturing high-grade electrodes was always regarded as a secret, of which only a few had definite knowledge.

Sir Humphry Davy, in 1800, was probably the first to employ carbon electrodes in connection with the electric arc. His electrodes were made of charcoal, and were simply points or rods cut out of carbonized wood. As a result, they were neither dense nor homogeneous. It can easily be seen that such carbons were rapidly consumed, not especially surprising when we consider the current and voltage he used. He employed the great battery of the Royal Institution, constructed after Wollaston's design, consisting of 2,000 pairs of plates, from which he obtained an arc of approximately 4 in. in length. It is highly probable that if we were to take some of our modern electrodes and subject them to such an arc, they, too, would be quickly consumed, for oxidation of carbon at the temperature reached in the arc is very rapid.

Foucault was one of the first to make use of "deposited carbon," or the coke that condenses on the inside of gas retorts. As early as 1846, however, Staite and Edwards patented a process of making carbon electrodes from pulverized coke and sugar, the mixture first being molded under a high pressure, and the shaped mass later baked at a white heat. The electrodes were then dipped in a concentrated sugar solution, the assumption being that the sugar would enter the pores and make the mass denser after a second

baking. About the same time, Leonolt prepared carbons consisting of two parts of retort coke, two parts of wood charcoal and one part of liquid tar. The materials were worked into a paste, well kneaded, molded, pressed, covered with sugar or sirup, and subjected to a high temperature for 30 hours or more. Leonolt also tried, but with indifferent success, to purify carbons by immersing them in different acids before baking.

In 1850 Watson and Slater experimented on a similar basis and 7 years later Lacassagne and Theirs attempted to purify electrodes by immersing them in fused caustic soda or potash, in the hope that they might thus change the silica in the carbons to soluble silicates. After fusing, the electrodes were steeped in hot water and exposed in a porcelain tube to a current of chlorine gas. It was supposed that the various earths not affected by the soda or potash would be converted into volatile or soluble chlorides, thus yielding a purer carbon.

Not long after these experiments, which were of no practical value, Curmer conceived the idea of making carbons of a mixture of lampblack, benzine and turpentine. This mass, after being kneaded, pressed and baked, left a porous coke, since the benzine and turpentine volatilized in a large measure during the baking process. Curmer attempted to increase the density of these electrodes by saturating them with resins and subjecting them to a second baking.

Jacquelain made carbons by using the hydrocarbons obtained in the distillation of coals, turf, etc., and also from the products resulting from the carbonization of these materials in sealed vessels. He obtained fair results, but never worked out a practical method or attempted to engage in the industry commercially.

Gaudin worked on electrodes which he made of lampblack. At that time, however, the price of lampblack was so high that he was obliged to seek some other material. He heated resins, pitch, tars and oils in closed vessels, and

obtained sufficiently pure carbon upon their decomposition. The volatile products of these substances were condensed and collected to be used again in mixing. He proceeded by pulverizing the carbon left after the decomposition and mixed it with a certain percentage of lampblack, using the condensed volatile products as binding material. This mixture was well kneaded, and molded with steel molds under the pressure of a powerful hydraulic press. The electrodes, after being baked, were considered to be superior to those in commercial use at the time.

From a commercial point of view, Carré appears to be the first to have had conspicuous success in producing carbons. He may justly be considered the founder of the industry.

The undeveloped state of electric lighting at the time had a great influence upon the work of these early investigators. It will be observed, however, that they were not far out of the way and that present-day practice differs from theirs only in that manufacture is assisted by more perfect mechanical methods.

When Carré studied the problem, the Gramme machine had just appeared and a host of inventors were struggling to construct a good arc lamp. There were demands for a good carbon that was practical in every respect, so that on the whole the time was very favorable to the founder of the arc-lamp carbon industry. It is interesting to read Carré's own account of this work:²

“The superiority of artificial carbons for various experiments and the possibility of purifying, with alkalis, acids, aqua regia, etc., the carbonaceous powders that enter into their composition led me to seek some means of producing them economically. By moistening the powders, either with sirups or gums, gelatine, etc., or with fixed oils thickened with resins, I succeeded in forming pastes sufficiently plastic and consistent to be forced into cylindrical rods

² Carré, *Compt. rend.*, Feb. 19, 1877.

through a drawplate placed at the bottom of a powerful compression apparatus of about 100 atmospheres. Carbons are now manufactured by this process and I have at various times presented some of them to the Société d'encouragement.³

"These carbons have three or four times the tenacity and are much more rigid than retort coke; cylinders of 10 mm. diameter and 50 cm. in length may be used without any danger of splintering during a break in the circuit. They may be as easily obtained in the slenderest diameters (2 mm.) as well as in the largest. Their chemical and physical homogeneity gives great steadiness to the arc, their cylindrical form, combined with the uniformity of their composition and structure, causes their cones to continue as perfectly shaped as if they had been turned in a lathe, and therefore there are no occultations of the point of maximum light like those produced by the projecting and comparatively cold corners of retort carbons. They are not liable to the inconvenience of flying into splinters when first lighted, as the others are, in consequence of the great and sudden expansion of the gas contained in their intercellular spaces which sometimes exceed 1 c.c. in capacity."

Carré's carbon mixture, which was patented January 15, 1876, was as follows:

Very pure coke, finely pulverized	15 parts
Calcined lampblack	5 parts
Sirup of sugar	7 to 8 parts

The whole mixture was well pounded together, kneaded and worked into a hard paste. It was afterward pressed through a drawplate by a hydraulic press and the carbons or rods piled into retorts, where they were baked at a high temperature.

³ Carré, Bull. de la Société d'encouragement pour l'industrie nationale, 1877. H. Fontaine, "L'Eclairage Electrique," 1877.

The general operations in the manufacture of electrodes have remained practically the same for the last century. Thus Carré has described the crude beginnings of the industrial operations of calcining, grinding, mixing, shaping (either molding or extrusion) and baking. Improvements have been in every one of these, from the original crude coal-fired furnace with its low thermal efficiency and high fuel consumption, to the present highly efficient type of gas-fired continuous variety of multisection ring furnaces. It is a long step from the original calcining ovens, producing poorly shrunk coke, to the gas-fired continuous vertical retorts used in the modern electrode plant.

In 1899 O. G. Pritchard,⁴ an Englishman, published a series of articles upon the manufacture of carbon electrodes. His raw materials and equipment are interesting to look back to, if for no other reason than that today, only thirty years or so later, they would not be considered commercially feasible.

His raw material was foliated Ceylon graphite, which he purified by pulverizing to a fine powder and then treated with potassium chlorate and sulphuric acid. The sulphated and oxidized mass was further treated with sodium fluoride to get rid of silica as the volatile tetrafluoride. After calcination the material was ready for use. Pritchard used purified cane sugar, caramelized, as a binder, explaining that he had failed in attempting to use tar oils, gums, hydrocarbons and beet sugar for the reason that all these substances produced undue porosity after the carbons were baked. He was unable to find a satisfactory measure for correcting this porosity.

Pritchard's mixture was pressed through an orifice at the bottom of a vertical hydraulic press at a pressure of approximately 1,800 lb. per sq. in. The carbons were cut into the desired lengths by shears as the stream came out of the press. They were dried in an air-drying room and

⁴ O. G. Pritchard, "The Manufacture of Electric Carbons for All Electrical Purposes," The Electrician Publishing Co., London, 1899.

kilned in a very crude intermittent coal-fired furnace, much like those used at the present time for the small-scale manufacture of red brick.

In the United States there was a patent granted in 1858 to De Grasses B. Fowler of New York for the process of making carbon plates by mixing ground coke with tar, shaping the mixture under pressure in molds, packing the shaped material in lime and heating it slowly in an air-tight box to drive off the volatile matter. As the experimental arc light shown at Yale in 1871 used electrodes cut from retort carbon, it is not very probable that Fowler's patent was commercialized for other than battery plates.

David Thompson of Newark was probably the first American manufacturer. His first plant consisted of a small crusher, a mixing pan, a crude brick oven, some cast-iron molds and a hand-operated grinding and bolting outfit.

Charles F. Brush and Washington H. Lawrence of Cleveland began to experiment on the manufacture of carbon electrodes about 1877. As they had found other materials unsuitable, they investigated the use of petroleum coke, a source of supply of which they found within a mile or so from their workshop where the Standard Oil Company had for years burned it under the oil stills in an effort to get rid of it. At first they used the raw coke, pulverizing and molding it to shape in electrodes about half an inch square and a foot long. As these electrodes had an abnormal shrinkage after baking, Brush invented the process of calcination of the coke prior to its fabrication into an electrode. Brush also invented a hydraulic press to impart greater density (due to greater pressure applied during shaping) than was obtainable with the hand press which was first used.

By the year 1878, Brush was manufacturing electrodes on a commercial scale. It was electrodes such as these that Hall used in 1886 in his experiments which led to the commercial production of metallic aluminum.

Up to the end of the nineteenth century, practically all of

the work in the carbon industry had in view the development of a satisfactory electrode for arc lighting. It was only in 1897 that Heroult and Hardmuth in France, and Plania and Siemens in Germany started work on the development of suitable carbon electrodes for electric furnace work. They used anthracite coal for the first time as a raw material. Heroult manufactured electrodes in Canada in 1908 and in the United States in 1911.

A great deal of the credit for the development of the modern electric furnace electrode in the United States belongs to the National Carbon Company, which in 1906 began experimental work to develop a furnace electrode several hundred times larger than the largest arc light carbon of that date.

The last quarter century has seen a most remarkable expansion in carbon electrode manufacture. Jehl⁵ in 1899 lamented the fact that the center of the industry was at that time at Charlottenburg and Nürnberg in Germany, while there were so many other locations in the world with much greater natural advantages. He says: "There is no reason why England should not make high-grade carbons, why the United States, with its immense petroleum wells and natural gas springs, should not supply the world with all grades of carbons. Russia and other petroleum countries also have an advantage in starting carbon factories and supplying their own market; in fact, the whole carbon business seems to fraternize with the coal-gas manufacturers and petroleum distillers."

In the United States, in most instances, the industry has been dependent for its existence upon a source of cheap electric power for baking the electrodes, while in Europe the gas-fired furnace has been most generally used for baking purposes. In this connection, although not directly connected with electrode manufacture, the names of Mendheim of Munich, for his invention of the gas ring and chamber

⁵ Francis Jehl, "The Manufacture of Electric Carbons for All Electrical Purposes," The Electrician Publishing Co., London, 1899.

furnace; Escherich, for his gas-ring furnace; and Meiser, for his modification of Mendheim's furnace, first applied to the baking of pottery and then adapted to the baking of electrodes, deserve prominent mention in the history of the electrode industry. The Meiser (more or less adapted to local conditions) modification of Mendheim's furnace is largely used in the United States. It has replaced electric baking to a large extent, even in localities where power is cheap.

Thus it may be seen that the development of the carbon electrode industry has been along four lines: (1) Electric arc lighting; as this industry expanded carbon development attempted to keep pace with it. (2) Electrolytic manufacture — e.g., alkalies, chlorine, aluminum and magnesium. (3) Electrothermic work — e.g., calcium carbide, silicon carbide, graphite, etc. (4) Electric furnaces — e.g., electric steel; copper, brass and aluminum alloys, ferro-alloys; nitrogen fixation.

One of the most important and useful industrial developments of recent years has been the extension of the use of electric furnaces. This was greatly accelerated by war conditions, war demands and war prices. This growth carried along with it an expansion of the electrode industry due to research and operating investigations. In 1919 there was a shortage of electric furnace carbons. Overwhelming demands swamped the manufacturers, not because of the lack of raw materials, but rather because of inadequate manufacturing facilities.

The latest progress has been along the lines of much stricter specifications as to purity, resistivity, hardness and increased density of electrodes. The earlier workers tried to obtain higher densities by saturating the baked articles with binders and baking a second time. In the present day the end is reached by starting with higher density raw materials and calcining them in a manner which will increase this factor. One of the greatest plant problems of today is the maintenance of absolute uniformity of output.

The growth of the manufacture of carbon electrodes in

the last twenty-five years or so has been tremendous. In 1899 the total value of electric furnace carbon output was \$10,974;⁶ today the total annual value of furnace electrodes produced is well over \$10,000,000. Electrode production is now the most important branch of the carbon industry; the output of brushes, which formerly was of greater significance only reaches the annual value of \$6,000,000.

The bulk of the production comes from the aluminum industry, which makes electrodes for its own use; and two carbon manufacturers, making chiefly graphite and amorphous electrodes respectively. There are also a number of smaller concerns producing electrodes.

The bulk of the production is from the states of Pennsylvania and West Virginia and from the Niagara Falls district of New York. The largest plant is one in New York. The entire demand in the United States can be supplied by domestic sources.

The chief foreign producers are Germany, England, and France. Carbon products are made in most of the countries of Europe and in Japan.

It is a long cry from 1800 and the little black rods of carbonized wood with which Sir Humphry Davy struck the first electric arc, to 1928 and the National Carbon's mammoth furnace electrode, 15 ft. long, 30 in. in diameter and weighing over three and one quarter tons. But 128 years is a comparatively long time when it is realized that in our own country in less than one-fifth of that time our output of electric-furnace electrodes has increased in value from \$10,974 (in 1899) to well over \$10,000,000. And were we to include electric-furnace products in that comparison, the figures would be almost unbelievable!

RAW MATERIALS FOR ELECTRODE MANUFACTURE

As a carbon electrode consists almost entirely of elemental carbon, it naturally follows that the best starting point for

⁶ U. S. Census, 1900.

its manufacture would be a material which contained the largest possible amount of carbon. A raw material would be desired which consisted almost entirely of carbon. This condition is satisfied by those bodies which are known under the general name of carbonaceous substances and, as a matter of fact, practically all carbonaceous matters are, or have been, used in the manufacture of electrodes.

Before attempting a detailed description of the various raw materials, it may be well at this point to devote brief attention to the characteristics and desired qualities of the finished electrodes in order that the raw-material requirements may be better understood.

In general, commercial electrodes consist of elemental carbon, contaminated with more or less ash, depending upon the raw material used in making the electrode. The ash is composed of the oxides of silicon, iron, aluminum, calcium and in some cases of copper. The resistivity—i.e., specific electrical resistance—expressed in ohms per inch cube, varies with the ash content; the higher the ash percentage the greater the resistivity, other factors remaining unchanged.

Electrodes for electrothermic work serve as refractory conductors of the electric current and do not enter into the reactions taking place in the electric furnace or other apparatus in which they are used. The manufacture of calcium carbide is an example of an electrothermic requirement. In this case the raw materials are coke and burnt lime. These are cheap and impure, for the coke contains a large amount of ash. It does no harm, therefore, to use an electrode high in ash in the furnace, for the additional amount resulting from the consumption of the electrode would probably be decomposed by the heat of the furnace itself. In many cases of the electrothermic use of carbons, the impurities of the electrodes either do not get into the product of the furnace, or if they do, make no appreciable difference in the product. Thus a satisfactory electrode for electrothermic purposes may be high in ash, since its resistivity is

either unimportant or else can be sacrificed if, by so doing, a cheaper electrode may be employed.

Commercial electric furnaces are becoming larger and larger, using increased currents and doing more exacting work. In certain cases of electric steel, sulphur contamination from the electrode may be important; electrodes for this purpose are made of specially selected low sulphur coals. Modern tendency is to increase the conductivity of electrodes by the use of higher calciner temperatures, with the production of a greater degree of graphitization of the product. Low ash coals are selected as raw materials. Higher conductivity electrodes are demanded more and more to allow the use of greater amperages in the furnace.

In electrolytic work, however, the purity and resistivity of the carbons are important considerations. Smaller currents are used at much lower voltages, so that high resistivity means a greater power loss than in electrothermic work. Furthermore, the material of the electrode may enter into the reaction and its impurities be imparted to the product of the electrolysis. An example is the reduction of alumina to aluminum. In this case the impurities of the electrode, if present in too great amounts, cause serious contamination of the aluminum metal. Silicon and iron are particularly undesirable. It is desired that carbons for electrolytic use have a low resistivity and be as free as possible from contamination.

Raw materials for carbon-electrode manufacture may be divided into three classes according to the part they play in the process: (1) "Body" materials, which are the carbonaceous matters making up the bulk of the finished electrode. (2) Binders, which serve to hold together the finely ground particles of the body materials, and (3) other miscellaneous substances entering into the manufacturing process.

The composition of the various body materials which are, or have been, used in the production of carbon electrodes is shown in Table XXV. The figures given pertain to the materials as found in their untreated, commercial forms.

TABLE XXV

Material	Moisture per cent	Volatile Matter, per cent	Fixed Carbon, per cent	Ash per cent	Specific Gravity
Coal:					
Anthracite.....	2.4-14.0	1.5- 8.5	65.0-85.0	6.0-18.0	1.5
Bituminous.....	1.8-19.0	6.0-40.0	49.0-79.0	2.8-19.0	1.36
Coke:					
Beehive.....	0.5- 1.5	0.3- 3.0	80.0-95.0	4.0-21.0	1.9
Byproduct.....	0.7- 3.0	0.6- 3.3	79.0-92.0	7.0-16.0	1.7
Petroleum coke.....	0.4- 2.0	4.0-18.0	82.0-97.0	0.5- 2.0	1.8
Retort and gas carbon	0.5- 2.0	4.0-13.0	88.0-97.0	3.0-10.0
Graphite, natural.....	0.5- 2.0	1.0- 7.3	78.0-92.0	7.5-19.7	2.0-2.5
Pitch coke.....	0.5- 1.5	4.0-12.0	85.0-97.0	0.3- 2.0
Wood charcoal.....	1.0-10.0	1.0-10.0	84.0-97.0	1.0- 4.0	1.6-1.8
Lampblack.....	0.6- 3.0	3.0- 7.0	90.0-96.0	0.6-10.0
Butts, amorphous, from electrothermic work.....	0.2- 2.0	0.0- 0.2	85.0-94.0	6.0-14.0	1.9-2.2

THE BODY MATERIALS

Anthracite coal contains a large amount of fixed carbon as compared with its content of volatile matter. The ash is incombustible mineral matter, consisting mostly of clay, silt or sand, more or less intimately mixed in the body of the coal. Selected low ash anthracite is used largely for electric-furnace electrodes. Little else other than anthracite coal and petroleum coke are used in making the large-sized electrodes for electric furnaces.

Escard⁷ gives the following data in regard to European practice in the purification of anthracite for use in making electrodes for the reduction of aluminum. "Anthracite in general contains more than 2 per cent of ash, of which at least 0.35 per cent is silica. This latter figure is inadmissibly high for the production of aluminum, but when purified

⁷ General Electric Review, Schenectady, N. Y., November-December, 1918.

such anthracite shows the following ash figure before and after treatment (anthracite is first degassed in one of the standard illuminating gas ovens, the gas being burned under the grate):"

TABLE XXVI

Constituents of Ash	Scotch Anthracite		Welsh Anthracite	
	Previous to Treatment, per cent	After Treatment, per cent	Previous to Treatment, per cent	After Treatment, per cent
SiO ₂	5.00	0.84	0.78	0.20
Iron oxides	1.06	0.25	0.32	0.12
Al ₂ O ₃	2.02	0.25	0.43	0.12
CaO and MgO	1.16	0.20	0.53	0.13
Total	9.24	1.54	2.06	0.57

The chemical treatment referred to by Escard consists of digesting the ground anthracite in a hot concentrated NaOH solution, and following this with a washing with a more dilute solution.

In the United States a much purer raw material can be obtained at a lower price than the cost of the purified anthracite would be, so that this method of purification is not used. In this country petroleum coke is the chief raw material for graphite electrodes which are made by graphitizing in the electric furnace.

Bituminous coal is high in volatile matter, containing a much smaller amount of fixed carbon in proportion to the volatile matter than the anthracite. It also runs high in ash. Since large losses are sustained in driving off the volatile matter in calcination and since the gases generated cannot usually be profitably disposed of by an electrode plant, bituminous coal is seldom used as a raw material. It has the further disadvantage of having a lower specific gravity than anthracite. Some of the first electrodes made for metal-

urgical work were prepared from a mixture of bituminous and anthracite coal, but the practice has since been abandoned.

Coke prepared from bituminous coal is high in ash content, high in fixed carbon and low in moisture and volatile matter. It is used in Europe for electrodes for electro-smelting, but to a much less extent in the United States. Coke is not employed in making electrolytic carbons.

Petroleum coke, the residue in the distillation of petroleum oil by the intermittent process, is the most important material for electrode making. It is a hard and brittle substance, of shiny, oily appearance, is very high in fixed carbon and low in ash. It is one of the purest forms of carbon available in large quantities. Its ash is probably due to the small amount of fine sand carried along mechanically or in suspension by the crude oil. The coke represents approximately 1 per cent of the original oil and from 8 to 9 per cent of the weight of the final residual tars after all of the other fractions have been distilled.

Sulphur is one of the undesirable constituents of petroleum coke, and is greater in coke from Mexican crude oils than from those obtained from other fields.

Not many years ago petroleum coke was merely a by-product — if not a waste — in the oil industry, and was disposed of by burning it under the stills. In recent years, however, the market price has greatly risen, and today the petroleum refinery regards it as a valuable commercial material. The quantity of petroleum coke being produced is growing smaller, however, because many oil distillers are changing over from intermittent to continuous or vacuum methods whereby no coke is produced. This change is causing electrode manufacturers to search the field for new sources for their raw material supplies.

The percentage of volatile matter in petroleum coke depends upon the temperatures reached in distillation. Present practice is to run the stills to as high a temperature as possible without actually damaging the bottoms of the

stills. Pyrometric control methods are not used nor is any attempt made to control the percentage of volatile matter in the coke produced.

After the run is finished, the still is allowed to cool for 4 to 6 hours. Workmen then enter through the manhole, their hands, head and feet wrapped in wet cloths, break off the coke with heavy iron bars from the sides and bottom of the still box, and unload it. Because of the excessive heat, the men can remain inside the still for only a short while. The coke is cooled by drenching with a stream of water.

Petroleum coke is received at the electrode plant in pieces varying in size from as small as 3 in. in diameter to chunks three or four times as large as a man's head. The coke consists of two portions, the main or upper part and beneath it a layer of denser material, called "shell," varying from eggshell thickness in some pieces to 2 to 3 in. This shell is the coke that was in contact with the sides and bottom of the still (see Fig. 58). It is higher in ash and soluble salt than is the coke of the upper portion, probably because the mineral matter of the oil gradually sank to the bottom of the still as the distillation proceeded and the shell, being the first coke made, formed around the mineral matter. Being nearer the source of heat and the bottom of the still, the shell was heated to a higher temperature and lost more of its volatile matter than did the upper portion.

Shell petroleum coke usually contains from 1 to 3 per cent of soluble salts, mostly sodium chloride. When coke containing shell is calcined in silica brick-lined retorts, the salts are volatilized and attack the brick-work by forming low-fusing sodium silicates. In order to save the retorts and lengthen their life, the shell is chipped off and separated from the main portion of the coke, to be calcined in special calciners by itself. The oil distillers formerly prepared coke in this manner, but in recent years have refused to ship anything but unchipped coke, as the cost and trouble of chipping was not justified by the price they received for the material.

The contracts of one of the largest electrode plants called for the delivery of approximately 50,000 tons of petroleum



FIG. 58.—SECTIONAL ELEVATION OF AN INTERMITTENT TYPE OIL STILL,
SHOWING COKE FORMATION

coke during the year. This amount is the result of the distillation of 5,000,000 tons, or 31,250,000 bbl. of crude oil.

Petroleum coke is used more than any other material in making the purest electrolytic carbons. The electrodes are low in ash and low in resistivity. For the lower grades,

where exceptional purity is unnecessary, petroleum coke is mixed with anthracite. This enables the manufacturer to turn out a cheaper electrode but of purer composition than if he had used anthracite alone.

Retort carbon, or "glance" coal, is a very dense form of carbon, produced by the deposition of carbon in the upper part of the retorts in the manufacture of coal gas. It exhibits the luster of a metal, is sonorous when struck and is a good conductor. Ordinarily it is rich in silica, the result of adhering fragments of brickwork and refractory pastes from the retorts. The amount of retort carbon on the market, however, is very small. A canvass of several hundred gas-manufacturing plants in the East was made to determine the amount of this material available. Quantities ranging from 1 to 25 tons per year were offered — this being the entire production of the individual gas works — at prices from \$20 to \$30 per ton. For most of the gas makers, the price received for the material would not have paid them for their trouble in accumulating it from the periodical cleaning of the retorts. The price asked was considerably higher than the market price of petroleum coke, a much purer substance.

Because of the difficulty of obtaining large quantities as well as its high price, retort carbon is seldom used in making electrodes. It finds its greatest use in the manufacture of carbon brushes, where its hardness and the sharp edges of its particles are employed to give a cutting grain to the texture of the brush.

Graphite. Graphite, of the natural variety, is not employed in the United States for the manufacture of electrodes, first, because of its high price (\$120 to \$180 per ton) and, second, because the artificial product, made directly by graphitizing electrodes in electric furnaces, as a result of its superior qualities, is given preference in practice.

Pitch Coke. Pitch coke has much the same qualities as petroleum coke. It is produced as a result of the destructive distillation of pitch, which comes mostly from coal tar. It

is low in ash and high in fixed carbon. At the present time it is not being produced in large quantities. Its production, however, is gradually increasing with the demand. In every place in which petroleum coke is now used it can be replaced by pitch coke. As the supply of petroleum coke grows less, due to the changed methods of oil distillation, its place will probably be filled by pitch coke. What is needed is the production of a pitch coke with a volatile matter so low (0.5 per cent) that it needs no calcination to prepare it for use in electrode making. This has been done, but not as yet on a commercial scale.

Wood Charcoal and Lampblack. These substances were used by some of the earlier investigators. They are low in ash and high in fixed carbon. Their high price, low density, and the fact that they are produced in relatively small quantities prevent their utilization in electrode making.

Butts. Butts are the unconsumed or waste portions of finished electrodes. They are usually high in ash. They are used in making electrothermic carbons, and are mixed in low percentages with petroleum coke for electrolytic electrodes. Usually, however, they are given a preliminary purification. As they are portions of electrodes previously baked, they need no calcining operation to prepare them for use.

TABLE XXVII

COMPARISON OF APPROXIMATE PRICES OF CARBONACEOUS MATERIALS, F.O.B. NEW YORK

Materials	Dollars Per Ton
Coal:	
Anthracite.....	8.00 to 9.00
Bituminous.....	3.50 to 4.00
Coke:	
Beehive.....	5.50 to 6.00
Byproduct.....	4.50 to 5.50
Petroleum coke.....	15.00 to 18.00
Retort carbon.....	25.00 to 30.00
Graphite.....	120.00 to 180.00
Pitch coke.....	Not on open market
Butts.....	20.00 to 40.00

A rough comparison of prices for the most important carbonaceous materials which are or may be used in electrode manufacture is afforded by Table XXVII.

BINDING MATERIALS

Binders for electrode making are divided into three classes; those which at ordinary temperatures are either (1) liquid, (2) semi-solid and (3) solid. The principal binding materials which have been used in the manufacture of carbon electrodes are:

(1) Liquid:

(a) Tars.

- (1) Retort-gas tar.
- (2) Oven-gas tar.
- (3) Water-gas tar.

(2) Semi-solid:

(a) Electrolytic pitch.

(3) Solid:

(a) Coal-tar pitch.

Chemical analyses of these substances are given in Table XXVIII.

The binders used are, in general, products of the distillation of coal. They are composed of elemental carbon and hydrocarbons in varying proportions. Their function is to hold together the finely ground particles of the body materials. Since the volatile matter of a binder is driven off in baking, the best binder, from the standpoint of the finished electrode, would be the one that had the highest coking value; or, in other words, loses as little as possible during calcining.

The earlier investigators used many different viscous matters to hold together their carbonaceous materials. These included caramelized sugar, sirups, molasses, resins, turpentine and various products from the distillation of organic substances.

TABLE XXVIII
CHEMICAL ANALYSES OF BINDERS USED IN
ELECTRODE MANUFACTURE

Material	Melting Point Deg. C.	Viscosity (MacMichael) (Seconds per 100 Revolutions)	Free Carbon per cent	Coking Value per cent	Softening Point Deg. C.
Coal-tar.....	Liquid	3-15	7-25	10-30
Retort-gas tar.....	Liquid	5-30	20-40	40-65
Oven-gas tar.....	Liquid	3-15	12-20	15-30
Water-gas tar.....	Liquid	3-8	2-5	10-20
Pintsch or oil-gas tar.....	Liquid	25-30	25-35
Electrolytic pitch.....	Semi solid	3-25	15-25	20-35	20
Pitch:					
Soft.....	50-70	3-35	15-25	20-35	35-60
Medium.....	70-90	15-40	25-35	30-40	50-80
Hard.....	90-140	20-250	30-50	35-55	80-115

Viscosity is more or less a measure of the binding power of a material. Viscosities are not absolute figures (unless absolute viscosities are used, reported in dynes per centimeter) and serve only as comparisons, one to the other. A binder with a high viscosity will tend to have a greater cohering power than one with a low viscosity. In measuring viscosity, either the Sturmer, also known as the MacMichael, or the Engler types of instrument are most commonly used.

Coal Tar. This material is too well known to require any extensive description of its properties. It is a black, viscous liquid, composed largely of hydrocarbons, with a low percentage of "free" or elemental carbon. It varies greatly in composition, and may better be classified according to its method of production into retort-gas tar and oven-gas tar. Coal tar used in making electrodes is usually a mixture of tars from different sources. Its viscosity is low; in the case of some thin tars it can be measured only with difficulty in the MacMichael instrument.

Retort-Gas Tar. This tar is obtained as a condensation

product in the hydraulic mains, scrubbers or condensers in the manufacture of coal gas for illuminating purposes. It is less fluid and contains less of the lighter hydrocarbons, more naphthalene, anthracene and their accompanying oils and more free carbon than tars from other sources. The composition varies with the heats and coals employed. In general, the lower the carbonization temperature of any coal, the more fluid the tar and the lower its carbon content.

Retort-gas tar contains 20 to 40 per cent of free carbon and yields on distillation from 50 to 75 per cent of pitch, or if the distillation is carried all the way, 45 to 65 per cent of coke.

Oven-Gas Tar. This material is obtained in the distillation of coal in byproduct coke ovens. It is similar to retort-gas tar, except it is more fluid. It contains more of the hydrocarbons and considerably less free carbon, which latter usually runs from 12 to 20 per cent. The composition changes, of course, with the coal, type of oven and the coking temperature.

Water-Gas Tar. The tar obtained from the manufacture of carburetted water gas for illuminating purposes differs mainly from coal tar in the entire absence of tar acids and ammoniacal liquor, and in the small amount of free carbon present, which is usually less than 2 per cent.

Water-gas tar on distillation yields from 35 to 60 per cent of pitch, or, if carried further, 20 to 40 per cent of coke of the weight of the dry tar.

Pintsch or Oil-Gas Tar. This material comes from the manufacture of oil gas used for railway lighting. It is similar to water-gas tar, but contains much larger amounts of free carbon, frequently 25 to 30 per cent or even more.

Coal tar, being usually a mixture of some or all of the above tars in varying proportions, is largely used in the manufacture of molded electrodes where great pressures are required, sometimes running as high as 25,000 lb. to the square inch. Tar is never used alone as a binding material in making extruded carbons, since tar binder mixtures are

practically unextrudable. Dehydrated tars, containing less than 0.5 per cent of moisture, are mixed with pitch. Tar is often employed to lower the melting points of pitches, and in small percentages, to give a more plastic mix for extruded electrodes. Where high-density carbons are desired, its low coking value is a disadvantage. Its use produces an electrode high in porosity, since a large proportion of it is volatilized during the baking process.

Electrolytic Pitch. This material is the result of the partial distillation of tar, in which only the lighter fractions are driven off. It is semi-fluid at ordinary temperatures and its properties are intermediate between those of tar and pitch. It is higher in free carbon and has a higher viscosity than tar. For a number of years it was used in some localities for making molded carbons but is no longer produced in large quantities.

Pitch. Pitch is the residue obtained in the distillation of coal tar after all the light oils, intermediate fractions and heavy oils (creosotes, anthracene, etc.) have been distilled.

Pitches may be classified, according to their melting points, into (1) those which at ordinary temperatures are soft and easily melted, (2) those which are midway between soft and hard and (3) those which are hard and require a much greater amount of heat to convert them to a liquid condition. This division is purely arbitrary. Soft pitches run from melting points of 50 to 70 deg. C.; medium from 70 to 90 deg., and hard pitches from this point to 140 deg. or higher. Over a wide range of melting points, the free carbon content and the coking value will increase with the melting point of the pitch. The same holds true for viscosity. Neither of these generalizations applies, however, over small ranges of melting points.

In making extruded electrodes, pitches are used as binders, to the exclusion of practically all other substances. They are often employed, in small proportions, to stiffen the mix, especially in making molded carbons with a tar binder.

Pitches are made by three methods of distillation:

(1) Tar is distilled to a hard, "core" pitch of high carbon content and with high melting point (150 deg. C. or higher) and then "cut back" with tar distillates to give a pitch with the required melting point.

(2) Tar is distilled to the required melting point under vacuum by the use of steam in the still. The steam assists in removing the high-boiling oils and helps to prevent the deposition of coke on the sides of the still.

(3) Tar is distilled in direct-fired horizontal stills carrying on the process without steam or vacuum and letting the products of distillation pass off under the pressure at which they were generated.

For extruded electrodes, large-scale experiments have shown that pitches made by the second and third methods are superior to those made by the first. The selection of tar distillates to be used in thinning down pitches, carried to the full limit of distillation (method 1) is especially important, since it has been found that when creosotes or naphthalenes are employed for this purpose the resulting pitch is lacking in binding power. This defect is obviated only by the use of heavier distillates, such as "green" oils of a more viscous character.

Pitch is normally about two-thirds of the weight of the tar from which it was distilled. Its physical character is mainly dependent upon the temperature employed in distillation, but its ultimate chemical analysis is governed by the tars used in its manufacture and the quality and composition of the coal from which the tars were produced.

About the only other material entering into carbon making is so-called "summer" oil. This is a crude petroleum oil from which the lighter fractions have been distilled. Since it produces a more plastic mix it is often used as constituent of the mix for extruded carbons in order to cut down the pressure necessary for extrusion. It has no binding properties. When it is used it cuts back the pitch and lessens its binding power.

The carbonaceous materials are received at the plant in

gondolas and are usually unloaded into track hoppers, which in turn are emptied by pan conveyors. Coal is purchased in run-of-mine size, petroleum coke just as it was broken out of the still, and butts as they were produced in the electrode-consuming processes. The materials are given a preliminary crushing in jaw or roll crushers to a 3-in. size and either carried direct to the calcining operations or are placed in storage.

Tars are usually stored in underground tanks, to which they can be unloaded from tank cars. The same holds true for summer oil. Pitch is commonly shipped in box cars. It is in the sizes in which it was removed from the stills and must be given a preliminary crushing in a roll or gyratory crusher.

Materials as received are sampled for chemical analysis and these are prepared for the laboratory by the methods of the Bureau of Mines.⁸ The carbonaceous substances are analyzed for moisture, volatile matter and ash, if they are to be used for electrothermic carbons; and in addition, for iron and silicon if employed for electrolytic electrodes. Binding materials are tested for melting, and softening points if they are solid; viscosity, free carbon, and coking value.

CALCINERS AND CALCINATION

We now take up the first step in production — to discuss critically the calcination process and the equipment used therein. First, let us consider the process of calcining itself. It is sometimes defined as "the heating of a substance to a white heat." This probably is in keeping with the original derivation from the Latin *calcinare*, meaning "to burn like lime." In the more restricted sense in which the carbon-electrode industry uses the term, however, calcination refers to the heating of a carbonaceous substance to the temperature required to yield a material with a content of volatile

⁸ G. S. Pope, "Methods of Sampling Delivered Coal," Bulletin 116, U. S. Bureau of Mines.

matter not exceeding 0.5 per cent. Uncalcined materials are generally referred to in the industry as "green," implying that further fabrication is required.

There may be said to be four reasons why calcination of carbonaceous substances is necessary in electrode manufacture: (1) The green materials when ground cannot readily be bound together into an electrode of proper density. (2) They are difficult to mold or extrude. (3) They give off their volatile matter during baking, thus resulting in a very porous electrode. (4) They are poor conductors and have a much higher resistivity than the calcined material. Calcination causes an actual shrinkage in the volume of the carbonaceous substance. It therefore effects an increase in the specific gravity or real density.

The calciners used in the electrode industry are either developments of the industry and its close connection with electrothermic and electrolytic processes, or else are adaptations from the manufacture of gas for industrial or illuminating purposes. The electric calciners, or "shrinkers," as they are often called, are examples of the first class, and the Woodall-Duckam and Glover-West vertical gas retorts are examples of the second.

The electric calciners were the first to be used in the industry, and where electric power is cheap and abundant they possess certain desirable features. They produce materials of lower conductivity. Coal used in electrothermal electrodes is usually "shrunk" in electric furnaces so as to have a greater degree of graphitization as a result of higher temperatures. Each of the various types of calcining equipment is now to be discussed, with particular reference to those in American practice.

Intermittent electric calciners usually consist simply of upright cylindrical steel shells lined with a highly refractive firebrick and resting on a ring of refractory brick work. A diagrammatic sectional elevation is shown in Fig. 59. Single-phase alternating current, with a voltage range of 30 to 60, is supplied to the aluminum or copper busbars encircling the

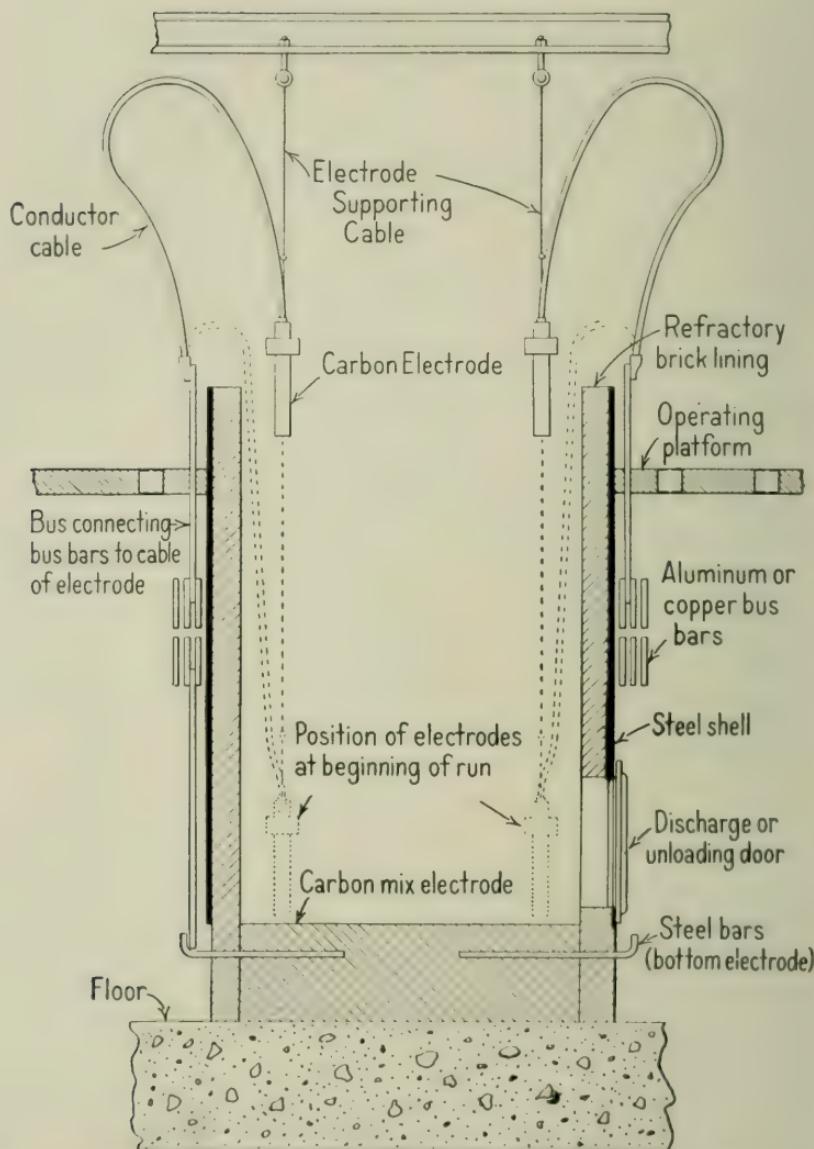


FIG. 59.—SECTIONAL ELEVATION OF INTERMITTENT TYPE OF ELECTRIC CALCINER

shell.⁹ Riser buses from the upper ring of busbars serve to carry the current to the flexible conductor cables connected to the electrodes. The electrodes, usually 6 to 8 in. in diameter and 42 to 60 in. long, are suspended from above by the use of steel wire cables. Strain insulators serve to insulate the cast-iron head of the electrodes from the cable and the overhead supporting beams. These electrodes are protected from rapid oxidation by sheet-iron casings filled with a tar-bound mix of finely ground carbon. The construction is shown in Fig. 60.

The lower ring of busbars supply current to the bottom electrodes through risers which consist of rolled steel bars, bolted on the outside of the shell to the riser buses. The bars usually 2 in. thick and 8 in. wide, are imbedded in a baked layer of a tar-bound carbon mix, which has been placed in the bottom of the shell while in a plastic condition and baked in place.

The arrangements and spacing of the suspended electrodes and the corresponding spacing of the bottom ones are shown in Fig. 60.

In operating the calciner the top electrodes are lowered so that they almost touch the bottom and thus cause an arc to be formed. Green material, fed in at the top of the furnace, falls to the bottom and is heated by the arc. When the material is heated sufficiently to conduct the current, the electrodes are gradually raised, the arc broken and heating continued through the electrical resistance of the charge. More and more material is fed in at intervals and the electrodes raised as each additional layer of the charge becomes conductive. In this manner the electrodes are gradually raised from the bottom to the top of the calciner during the course of 8 to 12 hours. Heating is then continued, usually for an additional 12 hours. After about 24 hours the top electrodes are raised out of the bed of heated material and the charge is permitted to stand or "soak" for 24 hours

⁹ For further electrical details see Yardley, "Production of Shrunk Coke in Electrode Manufacture," Chem. & Met. Eng., vol. 26, p. 321.

before it is unloaded. This is done so that the charge will develop the same heat in all portions of the material, and time will be allowed for the volatile matter to escape through the charge. Furthermore, it is necessary for the whole mass

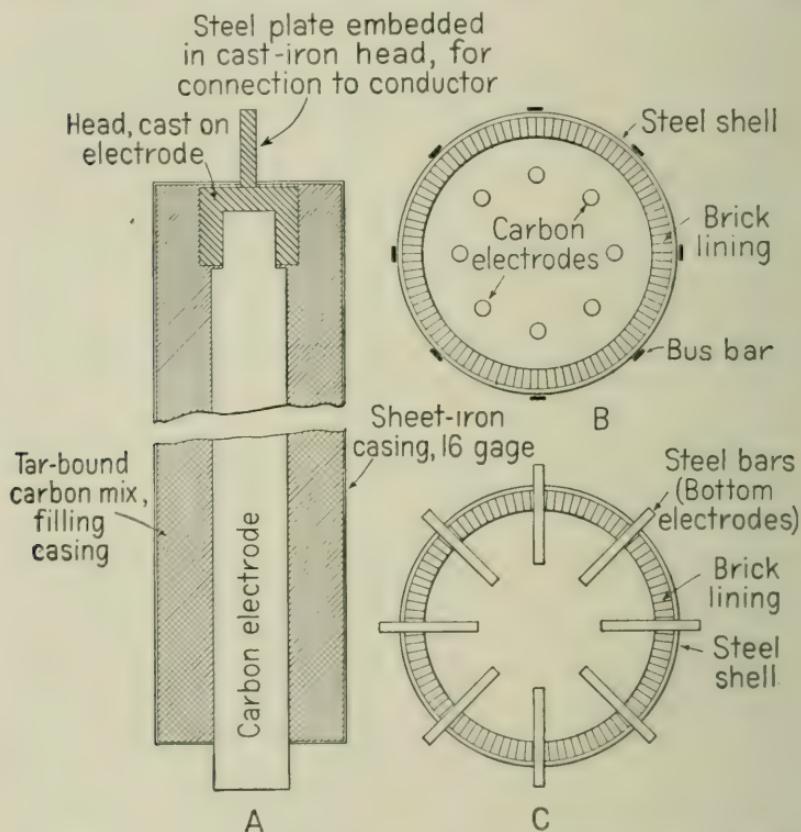


FIG. 60. — CONSTRUCTION DETAILS OF INTERMITTENT ELECTRIC CALCINER

A — sectional elevation of electrode.

B — plan of top, showing arrangement of electrodes.

C — plan of bottom, showing arrangement of steel bars in bottom electrode.

to cool somewhat before unloading. It has been found that the percentage of volatile matter of the calcined coke varies inversely with the "soaking" time; the longer the soaking time, the lower the volatile matter.

The charge is unloaded from the calciner by opening the discharge door on the side, breaking down the brick work, and hauling out the coke with long-handled rakes. As the material is still red hot, it is usually cooled by spreading it out on the floor in thin layers, or when necessary, sprinkling it with a fine spray of water. Wetting must be very carefully done, however, in order to avoid an excess that will not be evaporated by the coke. Moisture specifications for calcined coke call for a maximum of 0.3 per cent of water in order that when the material is finely ground it will not clog or "plug" the grinding mills.

The development of electric calcining units, particularly during the last 10 years, might well be shown by a brief review of the patents on the subject during that period. The developments have been along the lines of continuous furnaces, with attention given to the preheating of charges and recovery of the sensible heat of the calcined material as well as to the recovery of the valuable combustible gases produced as a result of calcination.

Attempts have been made at various times to convert the intermittent vertical type of furnace into a continuous one by providing it with some means of removing the calcined coke as it has been calcined. In most of these experiments there was little, if any, cooling of the coke and no sensible heat recovery; furthermore, the gas produced in the process was lost. These studies have resulted in only slight improvements over the original intermittent type of calciner.

Brown¹⁰ adapted the hollow electrode to electric calciners. One of his earlier furnaces consisted essentially of a hollow electrode located at the top of the furnace and passing through the cover, through which the material to be calcined is fed. There are two solid electrodes set horizontally through the side walls of the furnace. The radiated heat of the charge undergoing calcination is made use of by causing green material to pass on the outside of the material

¹⁰ John W. Brown, U. S. Pat. 1,067,795 (July 22, 1913).

part between the inner and outer shells of the furnace before being placed in the heating zone.

Brown next expanded the idea of using a high temperature and exposing the material to this temperature for only a short time by making the passage through the furnace very rapid.

In 1915 Brown ¹¹ patented an electric calciner which was continuous in its operation and recovered the gaseous products of calcination by a suction system. The charge enters the furnace from the hoppers at the top, dropping down through the opening between the upper electrodes. It is calcined during its passage between the upper and lower electrodes. The lower electrodes are hollow and serve as a means of entrance for blowing in gases drawn off at other portions of the furnace. These gases cool the electrodes and in their upward passage after being heated in the heating zone serve to preheat the cool uncalcined coke. The calcined coke is removed at the bottom of the chamber by a conveying apparatus.

Later a furnace ¹² was brought forward which was continuous in operation, recovered the gases resulting from calcination and used these gases to reclaim heat from the calcined coke and preheat the green charge. Essentially the unit consists of a brick shell in which there is an upper and lower electrode. The charge enters through an opening at the top and passes by the upper electrode into an inverted conical shaped chamber which is carbon lined, then into a restricted cylindrically shaped chamber, also carbon lined, where most of the calcining takes place. Dropping from here into another carbon-lined chamber shaped like the frustum of a cone, the charge finally passes to a conveyor mechanism which removes the material from the furnace. Calcining takes place as current is introduced into the furnace through the upper electrode. The calcined material is cooled by coming in contact with gases blown in through

¹¹ U. S. Pat. 1,143,940.

¹² U. S. Pat. 1,147,703.

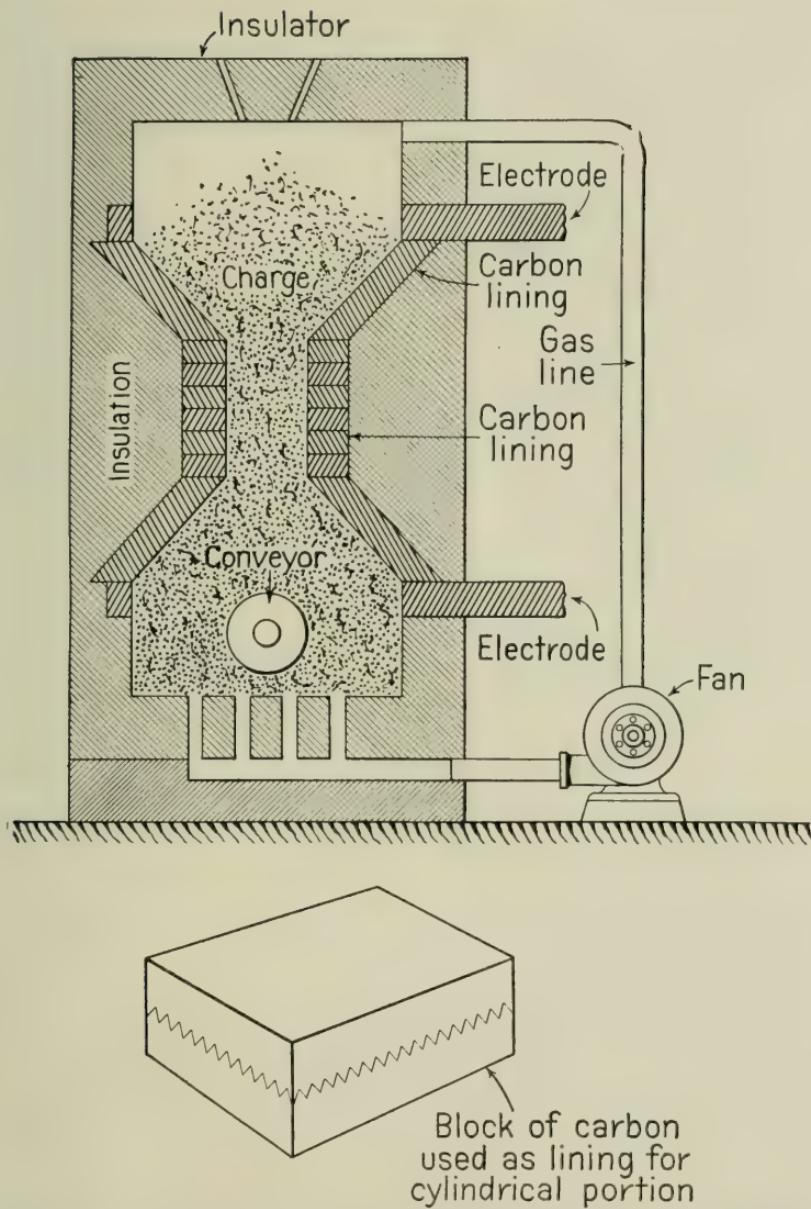


FIG. 61.—ANOTHER EXPERIMENTAL DEVELOPMENT OF ELECTRIC CALCINER

the bottom of the furnace. The gases in their upward passage cool the heated material, but are themselves heated at the heating zone. The heat they adsorb at this point is transferred to the cold green material through which the gases rise, thus preheating it.

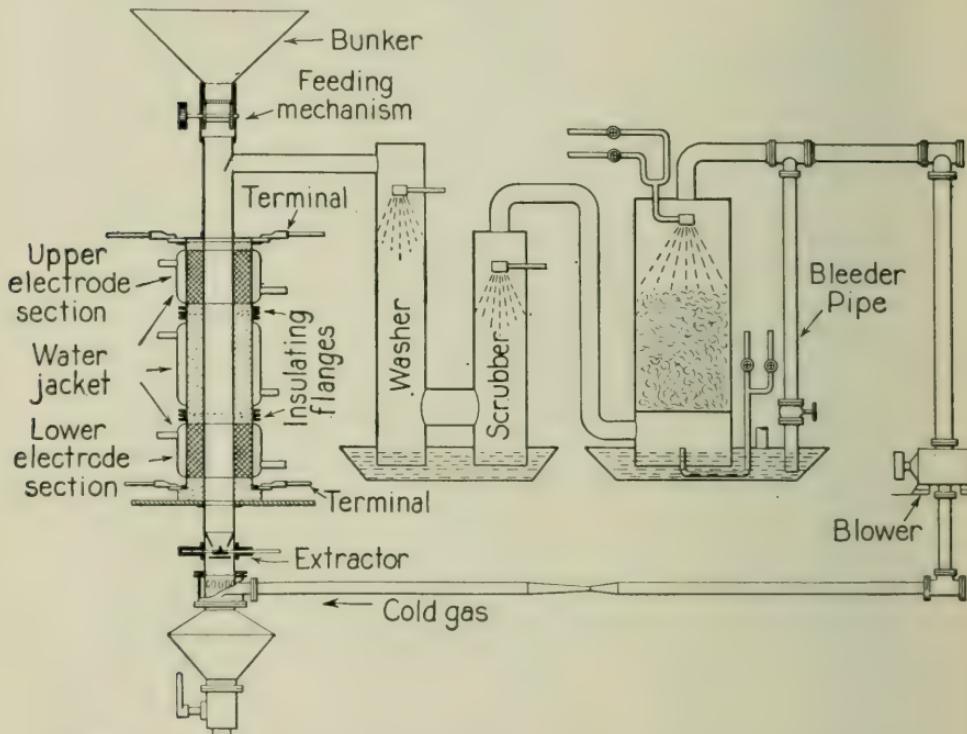


FIG. 62.—SECTIONAL ELEVATION OF A RING ELECTRODE TYPE OF ELECTRIC CALCINER

At various times patents ¹³ have been granted for furnaces in which portions of the charge were burned in order to preheat the materials before calcination and also to lower the cost of the process by reducing the amount of electric power consumed.

Probably the most important patent on the subject is that of William Hoopes for a ring-electrode, continuous-

¹³ U. S. Pats., 1,177,680 and 1,184,817.

type calciner.¹⁴ This type provides for continuous operation, recovery of the sensible heat of the calcined material, recovery of the gaseous products of the process and preheating of the uncalcined material. A diagrammatic drawing is shown in Fig. 62.

The furnace is of the vertical type, made up of three flanged sections. These sections are insulated from one another and the upper and lower ones lined with carbon electrodes or other carbon material. The middle section is provided with an insulating refractory brick lining. The heated portions of the shell are jacketed for water cooling. Material to be calcined is fed into the furnace continuously through the top. Gases arising from the expulsion of volatile matter pass off through an offtake at the top. A tee in the pipe allows some of the gases to be returned to the furnace at the bottom after the gases have been scrubbed, cleaned and cooled. The cold gases in passing up through the calciner cool the descending coke, pass through the heating zone between the upper and lower electrodes and cause a more even distribution of the heat. In passing off at the top, since the gases are now very hot, they heat the descending cold green materials and cause them to become conductive by the time they reach the zone of electric heating. Coke is extracted mechanically at the bottom.

Practically all of the types of electric calciners mentioned use single-phase alternating current. In the movable electrode type care must be taken that all of the electrodes carry nearly the same amount of the current, otherwise one portion of the charge will be overheated and another not heated enough. Due to the negative temperature coefficient of resistance of carbonaceous materials, the tendency during calcination is for the current to follow the path first established.

WOODALL-DUCKAM VERTICAL RETORT SYSTEM

The Woodall-Duckam retort for calcining carbonaceous materials is an adaptation from the gas industry for which

¹⁴ U. S. Pats. 1,366,457 and 1,366,458.

it was originally designed. It was first introduced in England in 1903 and in this country not long afterward.¹⁵ Coke or coal is fed through a hopper at the top of a vertical retort, heated on the sides. The speed of descent is so regulated that the coke is gradually calcined in its passage through the retort. The material is heated as it descends, and the gases from the volatile matter are evolved as the material reaches the proper temperature zones. The gases ascend, and are taken from the top of the retort. Thus the process is really one of fractional distillation.

The amount of material fed to the retort and the rate at which the charge descends are automatically governed by the rate the coke is removed from the bottom of the retort.

The retorts are rectangular and tapered from the top to the bottom. The retorts' walls are formed of tongue-and-groove bricks, paneled out at the back so that the heat is readily conducted to the charge. The heating flues are vertical, the division walls of the bricks being bonded into the walls of the retorts and also into the back walls of the flues.

The gas from the producer (either built in or an outside one) or else calciner gas from the operation of the retort, and the secondary air from the recuperator are admitted at the top of the vertical flues and burn downward. The secondary air passes around the lower end of the retort before it enters the recuperator. As now built, this recuperator is of box construction for the waste gas with the air baffling on the outside. The temperature of the secondary air is raised almost to that of the waste gases. Dampers are provided at the bottom of the retorts so that the pull can be regulated to both sides of each retort. Main dampers are provided on the waste gas outlet of the recuperator. Regulating dampers are provided on the gas and secondary air flues to each pair of retorts.

In shrinking petroleum coke in these retorts, temperatures

¹⁵ The author is indebted to J. S. DeHart, Jr., of the Isbell-Porter Co., of Newark, for the use of cuts illustrating the Woodall-Duckam system.

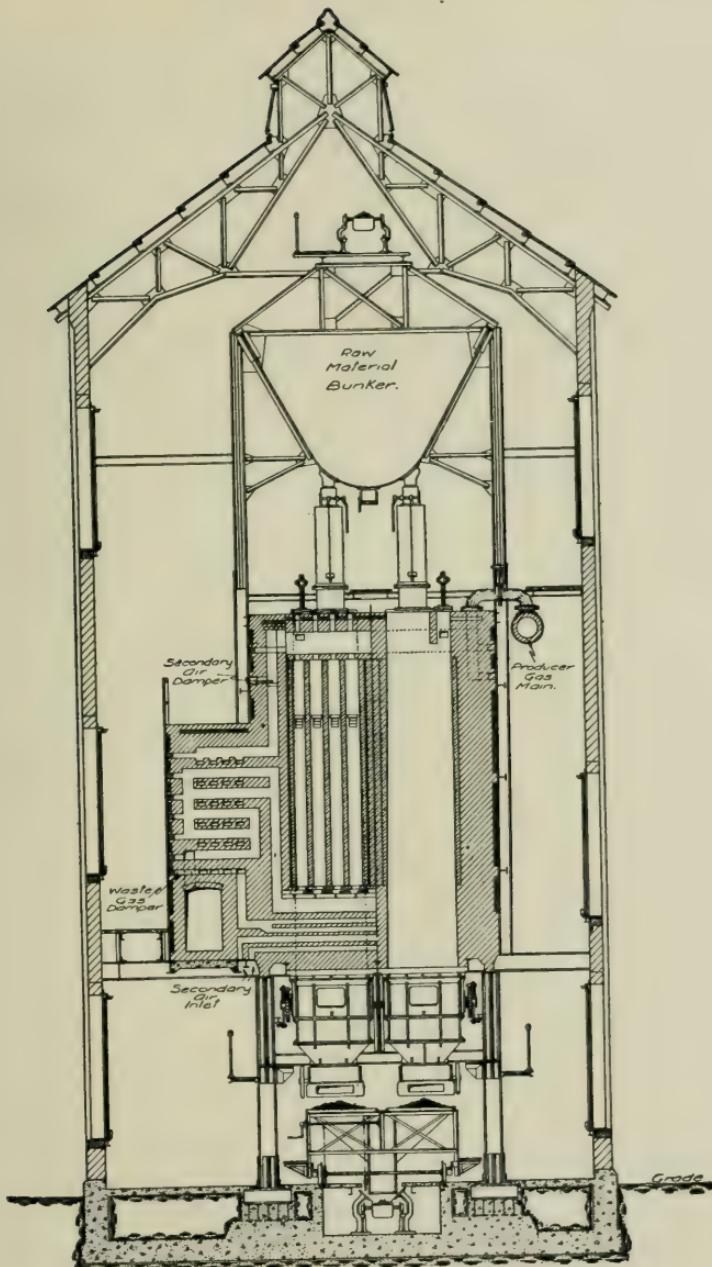


FIG. 63.—SECTIONAL ELEVATION OF TYPICAL INSTALLATION
OF WOODALL-DUCKAM CALCINERS
(Courtesy Isbell-Porter Co.)

of 1,050 to 1,250° C. are maintained, resulting in waste gases in the recuperators with temperatures of 650 to 850° C.

In the Woodall-Duckam extractor the coke is cooled by the water jacket before it is discharged. Figure 63 shows the sectional elevation of a typical plant for the calcination of petroleum coke such as is built by the Isbell-Porter Co. of Newark, N. J., which holds the Woodall-Duckam rights in this country. The plants are built either with or without an internal gas producer. When petroleum coke is used, much lighter gas is given off than with coal so that the bricklined gas main may be substituted for the more complicated hydraulic main generally used in the calcination of coal.

The temperature of the combustion chambers is highest at the top where the heat is most readily adsorbed by the cold material, and lowest at the bottom where the charge is completely calcined.

GLOVER-WEST VERTICAL RETORT SYSTEM

The Glover-West system of vertical retorts was based on patents granted in 1905 to Young and Glover. In basic constructional details these retorts resemble those used on Scottish oil shales. In 1909 the present Glover-West system was introduced into England. As in the Woodall-Duckam system, the calcination is continuous, but the methods of arranging for this vary in some detail. In the first place, the retorts are oval in section, instead of rectangular, and are built up of concentric fireclay rings. The bottom 3 ft. of each is composed of cast iron or special silica blocks and forms a regeneration chamber for the secondary air entering the producer. The passage of the gas from the retorts may be followed in the Fig. 64. An outlet is provided at the base of each coal-feeding hopper, whence the gas is conducted by a 7-in. pipe to a dry main. Each outlet pipe is fitted with a valve which is brought into use when a retort is out of action for surfcuring purposes.

The coke extraction is continuous and governs the rate at which coal is delivered. The extractor consists of a slowly

revolving vertical worm, driven at a speed of one revolution in about 35 to 40 minutes. The extractor is built in two halves so that one half may be removed and the retort readily inspected. The speed of the extractors is adjustable. Dropping from the extractor, the coke passes into a chamber fitted with a self-sealing lid and is removed from this at

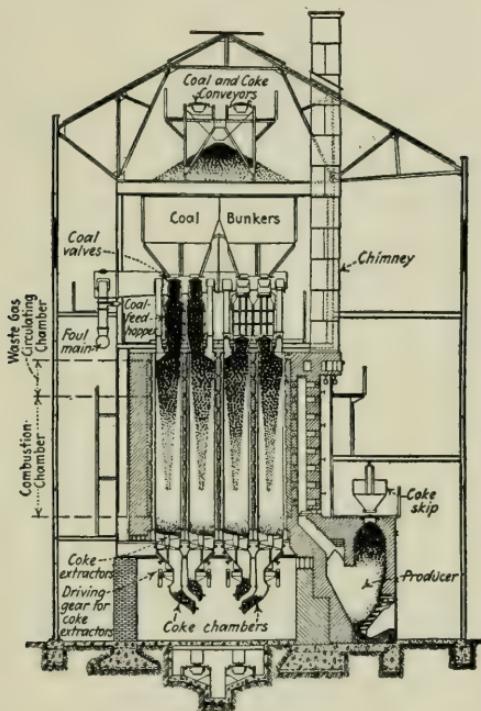


FIG. 64.—SECTIONAL ELEVATION OF GLOVER-WEST VERTICAL RETORT SYSTEM

intervals of about 2 hours. The system of heating the retorts differs from that of the Woodall-Duckam in that combustion takes place toward the bottom of the retorts and the waste gases pass around the upper portions into the horizontal circulating chambers before finding their way to the chimney. On account of the cooling action of the secondary air passing around the base of the retort, no water

quenching is needed and the coke is discharged from the lower chambers practically cold.

The retorts are heated in a series of superimposed chambers and the heats can be varied at will. The chambers are divided into three portions — the top or waste gas circulating chambers, the middle or heating chambers, and the bottom or regenerator chambers.

The calcined carbonaceous material is tested for volatile matter content by the standard method. The specification for volatile matter limits it to a maximum of 0.5 per cent. Moisture determinations are also made, for the specification allows only 0.3 per cent moisture. Resistivity is determined on ground samples (screened between 35 and 100 mesh), by measuring the drop in voltage at a constant amperage through a definite volume of the material. From this the resistivity is calculated. Usual specifications call for a maximum of 0.05 ohm per inch cube.

In general, due mostly to the higher temperatures reached in electric calcining than in gas-fired calciners, a denser coke or calcined product will be produced in the electric calciners. The advantage of gas-fired units lies in their lower operating costs, aided by the fact that they can use the gases driven off in calcining to heat the retorts, so that there will be practically no power cost. In electric calciners there is a tendency to graphitize partly some of the charge and in this manner produce a calcined product of lower resistivity than would be possible with gas retorts.

The basis of the finished electrode may be said to lie in the proper calcination of materials. Without it the arts of the expert carbon maker are of no avail.

GRINDING, MIXING AND SHAPING

The next step in the production process is that of grinding. The calcined materials (coal, coke and petroleum coke) are delivered from the calciners in sizes varying from fines to the largest pieces that will pass through a 3-in. screen.

To obtain the greatest density and highest tensile strength

in the finished electrode, it is necessary for the pulverized material to be graded properly — that is, to be composed of a mixture of large and smaller particles in a definite proportion rather than entirely of uniformly sized particles. The theory is that the smaller particles fill in the interstices between the larger ones and thus reduce the porosity of the mass and also increase its density. It can be easily shown that the porosity is the same in a mass of round particles of the same size, regardless of their dimensions.

Pulverizing is done with either of two ends in view: (1) To obtain the desired or as near as possible the desired grading by grinding all of the material in a mill which has been arranged to give the specific grading, or (2) To obtain the desired grading by screening the differently sized components of the pulverized material into various divisions and later building up a second mixture of the proportions desired.

Both of these methods are used, the latter principally in Europe and less in North America. The second method tends to become complicated, as there is likely to be, at some time or other, an excess of some division of the pulverized material after screening. The second method involves a number of tanks for the screened material, a number of weighings and proportionings of the separate divisions of the screened material and a remixing to cause the large and small particles to be uniformly distributed throughout the mass.

Inasmuch as most electrodes are made of at least two carbonaceous materials, it is not necessary to go to the trouble of separating the various sizes of pulverized materials. Grading of the particles may be accomplished by pulverizing one material finer than the other, and mixing them in the proportions desired.

The unit largely used in American practice for pulverizing the calcined material is the roller pulverizer with air separation. This machine requires a feed of material of approximately 1-in. size for efficiency operation at maximum capacity. It is usual, therefore, to pass the calcined material

through a roll crusher in order to break it down from 3- to 1-in. pieces, preparatory to sending it through the pulverizing mill. These crushers are corrugated rolls, equipped with reciprocating plate feeders.

In the newer electrode plants, the roller mill has been replaced by tube or ball mills.

Present practice calls for much greater attention to screened aggregates than formerly. Screens of the inclined mechanical type, some of them electrically vibrated and others mechanically shaken, are now the usual equipment for obtaining aggregates of the proper and desired screen analysis.

The modern grinding sections of electrode plants are fully and completely equipped with dust collection devices on the end of the air separation apparatus. These dust collectors are of the mechanically shaken tube type, with periodic air reversals and tube shakings. The tubes are enclosed in sheet steel casings.

Butts, the unconsumed portions of used electrodes, constitute a large portion of the raw material of electrode plants supplying certain industries, such for instance as the reduction of aluminum. Butts are generally hard, tough and somewhat brittle. Their pulverization for re-use presents a more difficult problem than grinding petroleum coke. Former practice was to crush them first in a rotary crusher and then feed them to a ring pulverizer, a roller mill, or a tube mill. Under present practice greater capacity per machine is obtained by first cracking and crushing the butts in a jaw crusher, then after picking out metals and other contamination they are run into a rotary crusher and finally are fed to a roller mill.

Practice as to grinding pitch differs in the various plants according to the mixing requirements. Some plants obtain satisfactory results by merely coarse-grinding the pitch in a rotary or a gyratory mill after the material (as it comes from the still) has been broken up in a corrugated roll crusher. This method gives a ground product varying in size from fines to pieces passing through a 2-in. ring.

The second method is to fine-grind the crushed pitch in a mill of the swing hammer type. This yields a product all of which is smaller than $\frac{1}{8}$ inch.

The storage of great quantities of finely ground pitch is a difficult problem. If large masses are left undisturbed for several weeks, it will be found that the lower portions of the pile have regilated, or run together, much like ice when it freezes. The pile can be broken up only by pickaxes, air drills or blasting. For this reason it is common practice in electrode plants using finely ground pitch to grind only a single day's supply in advance.

Pitch dust, according to tests in the explosion gallery of the Bureau of Mines, is very explosive. This is due to its high percentage of volatile matter. The grinding of calcined petroleum coke and calcined coal, on the other hand, is attended with very little hazard, since these materials have had practically all of their volatile matter driven off.

Pulverized materials are usually stored in large inclosed steel banks, elevated from the floor and having outlets at the bottom. Material of this fineness flows very readily and accordingly leaks out through every small opening much as if it were a liquid. Two devices which are successfully used to control the flow of pulverized material of this sort are the "blast gates" or "coal cocks" made by the manufacturers of pulverized fuel equipment.

Soft pitch is melted prior to use or else a supply is kept in a melted condition. When tar is employed as a binder, it is usually thinned by heating so that it will flow more easily and can be more readily measured. Summer oil, another constituent of the mix, is usually stored in large tanks from which it is piped to the mixer room.

MIXING PRACTICE

Proportioning of materials is usually done by weight in the case of solid substances, and by volume in the case of liquids. The solid materials are drawn from their various

tanks and weighed into the mix box in the proportions desired. Experience with table proportioning machines has been generally unsuccessful because the dust is so lively that it would flow over the tables of the machine and would not assume a position of rest which is necessary for the operation of the machine. The dial type scale has been successfully used for weighing dusts. In operating this, a workman permits dust from one tank to run into the mix box until the required weight is obtained, and then closes the valve on one pipe and opens it for the supply of the next constituent, thus making the operation continuous until the mix is obtained. No matter how clever the workman was, some poorly proportioned mixes would slip through.

An improvement in proportioning mixes has come with the installation of automatic weighing machines. Separate scales are used for each material, each scale dropping its charge into a common hopper which empties into a mix box. They operate on the balanced beam principle, discharge through toggle mechanisms when they have weighed their charge, and after discharging, return to position for another weighing. They can be set for any number of successive weighings without interruption.

The weighed dust, along with the binder if it be hard pitch, is dumped from the mix box into the mixing machine. If the binder has not yet been added, it is poured or run in some time during the mixing. Mixes with pitch as a binder are not stored for any great length of time after being proportioned, as segregation may take place and make it difficult to produce an even and uniform mix.

The mixing machines are heated by steam jackets and have some sort of provision for loading and dumping of the charge. One type consists essentially of a steam-heated drum mounted on its side. Mixing is accomplished by rotating a central shaft with arms attached to it. The forward tilt of the arms, which during rotation carry the mix forward, finally discharges it through the door at the end of the drum. Another type is a modified design of the well-

known bread mixer. Propellers or fins on pairs of shafts interlace, the shafts revolving in opposite directions.

The object desired in mixing carbon is to use as little binder as possible and still have the material extrude from the die and not crush or fall to pieces. The condition which is desired in making a carbon mix is to cover each particle of dust with as thin a film of binder as possible, so that when the various particles come in contact they will be well bonded together. Theoretically it is possible to calculate the minimum amount of pitch necessary to accomplish this purpose and several attempts in this direction have been made by the National Carbon Company. The practical difficulties met with in carrying out experiments of this type are practically insurmountable, due to the inability to obtain the size of all the particles. Fortunately, however, an experienced mixing and pressroom foreman who has had the proper training, can gage the amount of binder in the mix he is using so closely that if $\frac{1}{2}$ lb. of binder per 100 lb. of mix is removed from the mix, it will cause the product to come from the extrusion press badly cracked.

Pan rolls are used both in this country and abroad for the purpose of obtaining a more uniform and denser mix than that given by the mixer alone. As far as the writer has been able to ascertain, they are not used for rolling a mix with a hard pitch binder.

The material is delivered from the mixers to the presses for the shaping of the electrodes. This can be done in two different ways. One is by placing the mixed material in a mold and subjecting it to great pressure. The other is to place the carbon mixture in a cylinder, and by means of hydraulic pressure force the mixture through a die or mouth-piece of the requisite shape. Electrodes made by the first method are termed "molded," and those by the second extruded or "forced." Both the methods produce products that are homogeneous and of low porosity. The molding process usually results in a higher density electrode.

Extruded electrodes are usually used for electrolytic work.

The reason for this is that it is easier to make the sizes of electrolytic carbons by extrusion, as only one or a few dies are needed, while many molds would be required to produce the same result by the molding process.

Due to the rapidity of the process, small electrodes are usually made by extrusion. Large electrodes can be made by both methods, those made by molding being preferred because of their higher density. Extrusion presses are now made so that electrodes as large as 36 in. in diameter can be produced by this process.

In the case of large electrothermic electrodes, the high density and low resistivity of the electrode are as important as when smaller currents are used.

The equipment usually used for molding consists of the dies of the shape of the finished molded article and upright hydraulic presses to compress the materials in the mold. The molds are made of steel, or in some cases of heavy cast-iron construction, for they must stand great pressure.

The mixed material is placed in the mold as compactly as possible with enough extra material as has been determined by practice to compensate for the compression and still have the finished article fill the mold. The mass is pressed to shape between the top and the plunger of the hydraulic press. It is stated that pressures as high as 25,000 lbs. to the square inch are sometimes used. Mixes for molding are generally made with pitch binders. The articles are removed from the mold as soon as they are cold enough to hold their shape, excess material is removed and the mold cleaned and lubricated for the next pressing.

Extrusion is a more rapid process than molding, requires less labor per ton of material produced when the same size is produced in quantity. Since most electrodes are made by that process, extrusion will therefore be considered in somewhat greater detail.

In making electrodes by the extrusion method the hot mix is first "slugged" in the slug presses. These are vertical hydraulic presses, an example of which is shown in Fig. 65.

The hot mix is placed in the mold or "pot," as shown in the illustration, and the material is compressed between the head and the plunger of the press. This operation serves only to shape the mix and give it a form in which it can be readily handled. The slug is removed from the pot and is sent forward to be fed to the extrusion press.

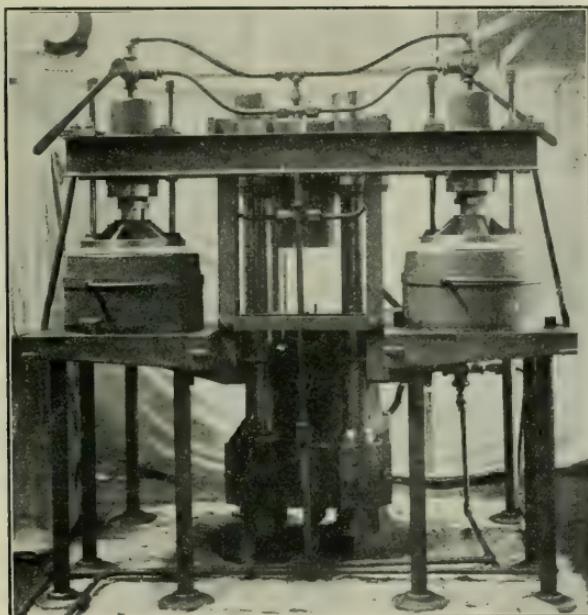


FIG. 65.—A VERTICAL SLUG PRESS
(Courtesy John Robertson & Co.)

Slug presses are normally operated at low pressures—that is, between 800 and 2,000 lbs. per sq. in. Often it is necessary to employ some sort of lever arrangement, to knock the slug out of the mold. As shown in Fig. 65, this is directly over a hole in the working table of the press, through which the slug drops out to the floor or platform beneath. Automatic slug presses, capable of much greater capacity and entailing a much less physical effort on the part of the workmen in slugging the material, are replacing the type of press here

illustrated. These are built with revolving tables, the pots being locked in place on the table. Three pots are used, one being filled with the material, another being compressed and a third discharged.

Slugs are made cylindrical in shape, the height being as great as permissible and still allow the slug to be easily handled. Slugging serves to remove occluded air and gas from the carbonaceous mass. The slugs are kept hot and are fed into the "mud" chamber of the extrusion press. This is the steam-jacketed cylindrical section of the extrusion press that serves as a loading chamber. An illustration of an extrusion press is shown in Fig. 66.

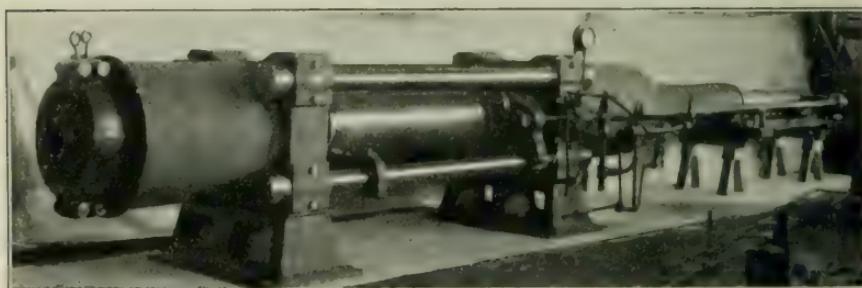


FIG. 66.—A 750 TON HORIZONTAL EXTRUSION PRESS
(Courtesy John Robertson & Co.)

Some plants make large square electrodes by molding in presses which are really slug presses adapted for continuous operation and a higher pressure range. The "pots" or molds are chained or joined together. Filling, pressing, and discharging are done simultaneously. Four pots are used and filling is stopped by the movement of the pots a quadrant at a time. Operation of some of these presses is at a rate as high as four per minute. No attempt is ordinarily made to hold pressure on the block for any appreciable period. The molded blocks are pushed out of the mold by an ejector arm which is yoked with and breaks with the pressure ram.

Extrusion or "plug" presses, as they are often called, are operated at hydraulic pressures as low as 1,200 lbs. per sq.

in., to as high as 7,000 lb., the variation being caused by different plasticities of the carbon mix. Operation is arranged to obtain mixes which extrude at approximately the same pressure. Opinions as to extrusion pressures favoring best results differ somewhat in different plants, but the usual range is between 2,000 and 4,000 lb.

The size and shape of the extruded electrode will naturally depend upon the shape of the die or mouthpiece. Tubes can be extruded by the use of a spider setting, placed in the throat of the mouthpiece. The length of the electrode is limited only by the capacity of the loading chamber of the press in terms of the volume of the electrode shape.

The maker of the large sized electrothermal electrodes now uses extrusion where the user demands that the possibility of electrode chunks' falling into his furnace be eliminated. Molded electrodes may crack at right angles to their length; extruded electrodes parallel to their length.

The carbons, after being pressed and shaped, are termed "green" to distinguish them from the finished and baked electrode.

Fig. 67 shows a typical installation for extrusion. An overhead monorail crane carries mixes in a mix box (B) to hoppers (H) on the third floor, located, one to a machine, directly over the mixing machines (M) on the second floor. The dust and binder have previously been proportioned in an adjoining dust storage building. The materials are mixed, and discharged from the machines into a dump car (C) traveling on tracks in front of the mixers. The dump car discharges into a hopper (S) feeding the pot (P) of the slug press (PP). The slug press discharges onto a platform (L), from which the slugs are conveyed on a roller carrier to the extrusion press loading table (LL). The slugs are loaded into the extrusion press (E), extruded through the mouthpiece of the press hot, cut to length by a cutting knife mounted on a table next to the die, and dropped into the cooling tank (C), which consists of a wood slat conveyor running under water. The green electrodes are discharged

from the cooling tank onto an inspection table, inspected, loaded onto tared trucks, and transported to the baking furnaces.

The mixer and press rooms are the heart of the electrode plant. The quality of the finished carbon is largely dependent upon the quality of the green carbon extruded. A good

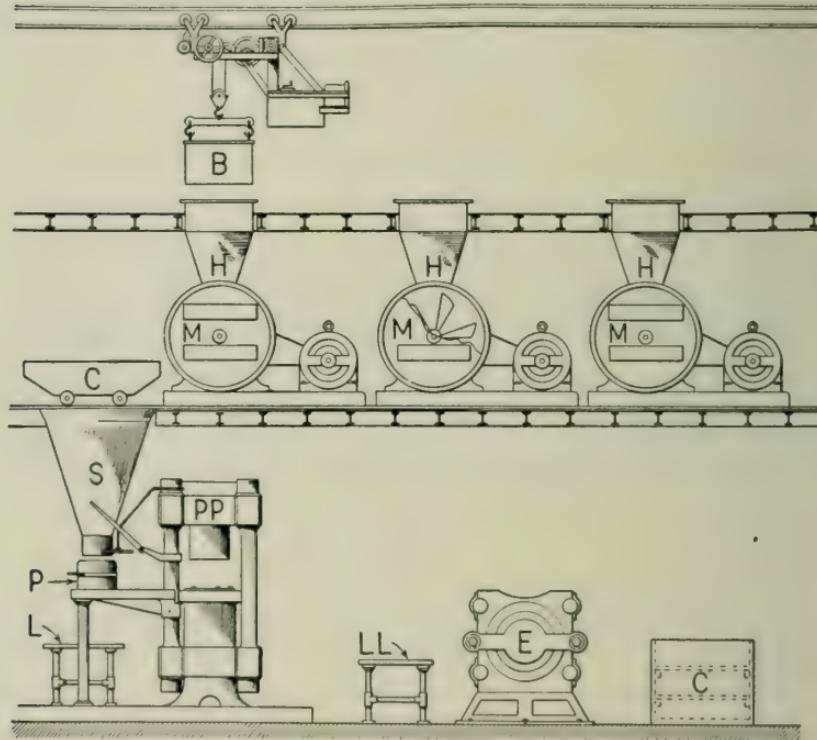


FIG. 67.—A TYPICAL INSTALLATION FOR EXTRUSION

green carbon will usually produce a good baked one if baking conditions are right. A poor green carbon will never produce a good product no matter how well the baking operations are conducted.

Mixing practice differs even in plants making the same kind of electrodes for the same purpose. Practically all mixing is accomplished by cut-and-try methods and the test

as to whether a mix is finished or not is to take up a handful of material and "feel" it. If it "feels" as past experience has shown the mixer man a good mix should, it is finished. It is practically impossible to proportion a mix on paper and have it actually work out in that desired manner.

Most of the difficulties of mixing are due to lack of uniformity of the binder. There is as yet no satisfactory method of determining the binding power of a binding material except actually trying it out. The binding power of pitches varies more or less with their melting points, but differences in the method of manufacture make it possible to have two pitches of nearly the same melting point with widely different binding properties. The thing of greatest importance about pitch and mixing methods is that the pitch be uniform at all times. A good carbon can be made of high-melting pitch; likewise a good carbon can be made of low-melting pitch, but if there occurs, in the course of the day's work, several batches of high- and several batches of low-melting pitch, naturally the carbons themselves will not be uniform in their characteristics unless the mixing and forcing conditions are changed accordingly.

While the melting point has the predominating influence on a mix, the fact that the insoluble residue, which is carbon also, has its effect should not be overlooked. Its effect is not as pronounced as the melting point, for it does not vary so greatly. Obviously a pitch with a high residue will have to be used in greater quantities with a given amount of dust than would be the case with a pitch of low residue, for this residue is finely divided carbon.

Good carbons can be made whether the pitch is finely ground, crushed or melted, but the actual mixing and forcing conditions will vary with each process. Naturally if the pitch is already melted it need not stay in the mixer so long to give a good mix, but there will be some difficulty in adding the pitch so as to keep it from coagulating or agglomerating when it touches the dust. To prevent this it would be necessary to have the dust at the same or nearly the same temper-

ature as the added pitch. Melted pitch can be added to a cold flour and a good mix obtained, although the chances are it would take a higher mixer temperature and a longer mixing time.

A good mix can be obtained by finely grinding the pitch and adding it to the mixer either with the flour or after the flour has been put into the mixer and become heated. A good mix can be obtained by using a pitch crushed in a gyratory crusher, as is the practice at some of the Niagara Falls plants, but here again the same mixing conditions must not be used as with pitch which is melted or more finely ground.

Inspection at the tables at the end of the cooling tanks separates the passable electrodes from those which go to the scrap pile. Good electrodes must be of proper density, have smooth outside surfaces, be free from cross checks or splits, contain no cores, unmelted pitch or foreign material, be cut to proper lengths, be cut square and be well shaped.

After the electrodes have been inspected and those of the defective types have been eliminated, the sound, well-shaped electrodes are piled on trucks, weighed and sent to the baking furnaces. Samples of each lot are taken for density determination and chemical analysis.

BAKING AND BAKING FURNACES

Baking has for its object the conversion of a highly resistant "green" electrode into a low-resistance finished product; the conversion of a material with qualities and properties which vary with temperature changes into one whose properties remain fairly constant over a wide range of temperatures; and lastly, the conversion of a material with low tensile strength into one which is strong and capable of withstanding hard service.

Baking accomplishes these results by a distillation-cracking action on the binder. As the temperature increases the binder successively softens, melts, loses its lighter constituents by distillation, and finally is converted into coke. At

the end of the baking process, even the coke has lost whatever volatile matter it may have retained during its actual formation. According to the speed of temperature rise in the process, the volatile portions of the binder may or may not be "cracked"—that is, broken down into simpler compounds and carbon. As the result of the coking of the binder, the whole mass of the electrode is held together very strongly. Each small particle that had been covered by a film of binder is bound to the adjacent particles by an extremely thin layer of coke.

The change that has taken place during baking is easily demonstrated. A green electrode, if struck on a stone or concrete floor, causes a sound much like a thud. The same electrode after baking, if struck in the same manner, gives out a resonant bell-like tone.

The furnaces used are of two kinds, those in which the heat for baking is generated by the electric current, commonly called electric furnaces; and those in which the heat for baking is obtained from the burning of a combustible gas, commonly called gas furnaces.

ELECTRIC BAKING FURNACES

The rise of electrode manufacture has paralleled that of the electrochemical industries. The electrochemical industries naturally gravitated to sources of cheap power, which were the great hydro-electric developments. Electrode plants soon located near their electrochemical customers and they themselves became users of cheap power for heating purposes. As a result, during the earlier stages of the development of carbon manufacture, the electric current was used entirely for electrode baking to the exclusion of other methods of heating.

The electric furnaces used for carbon baking are of the horizontal resistance type, heating the contents of the furnace by the resistance of the charge. They consist simply of two ends, which are brick walls in which the electrodes for carrying the current to the charge are supported, and two

removable sidewalls of brick set up by hand without mortar or cement. The bottom of the furnace is insulated by filling it with some cheap dielectric, such as broken concrete, gravel, brickbats, etc. The appearance of the built-up furnace is

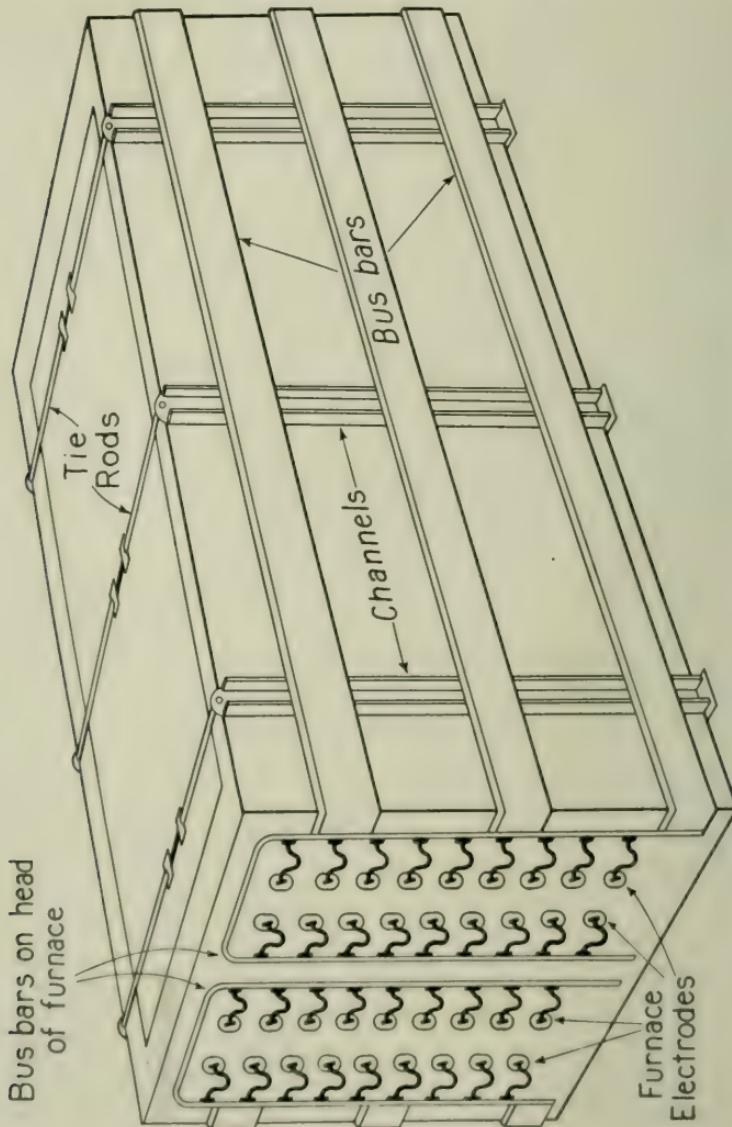


FIG. 68.—SKETCH OF ELECTRIC CARBON ELECTRODE BAKING FURNACE

that of a rectangular box. Furnaces usually are operated on single-phase alternating current at twenty-five cycles frequency with 30 to 60 volts.

The sketch in Fig. 68 shows the principal features of a standard baking furnace. Power is supplied from transformers to the furnace through copper or aluminum busbars, both heads of the furnace being connected by furnace busbars to the main set from the transformers.

DETAILS OF CONSTRUCTION

The sidewalls are of refractory clay brick, built in such a manner that the bricks in the wall "lock" one another in position by continuously crossing, layer after layer. Either one or both walls are torn down at the end of a run so that the baked carbons may be unloaded from the furnace. The sidewalls are held up and supported against undue pressure from the inside by channel irons placed at definite intervals. The ends of the furnaces are built of fireclay brick laid in place with mortar or cement.

Transformers used are normally of the single-phase, oil-filled type with a voltage range on the low side of 30 to 60 volts. The capacity of transformer used depends upon the size of the furnaces connected to it. Usually electrical connection is made so that four furnaces are "hooked up" to a single transformer. This is done so that the transformer may be operated at all times except when a change of connection between furnaces is being made. Switches are not provided for the furnaces, but only for the transformers. When a furnace is not "on power" (that is, not having power passing through it), the side busbars are removed so that the heads of the furnace are disconnected. Operation is such that one furnace of a group is always on power, the others are cooling, loading or unloading.

Either one or both sidewalls have been torn down during unloading. All old packing dust is removed from the furnace. Any electrode cable, clamp or busbar replacements are made before loading is started. The furnace is opened

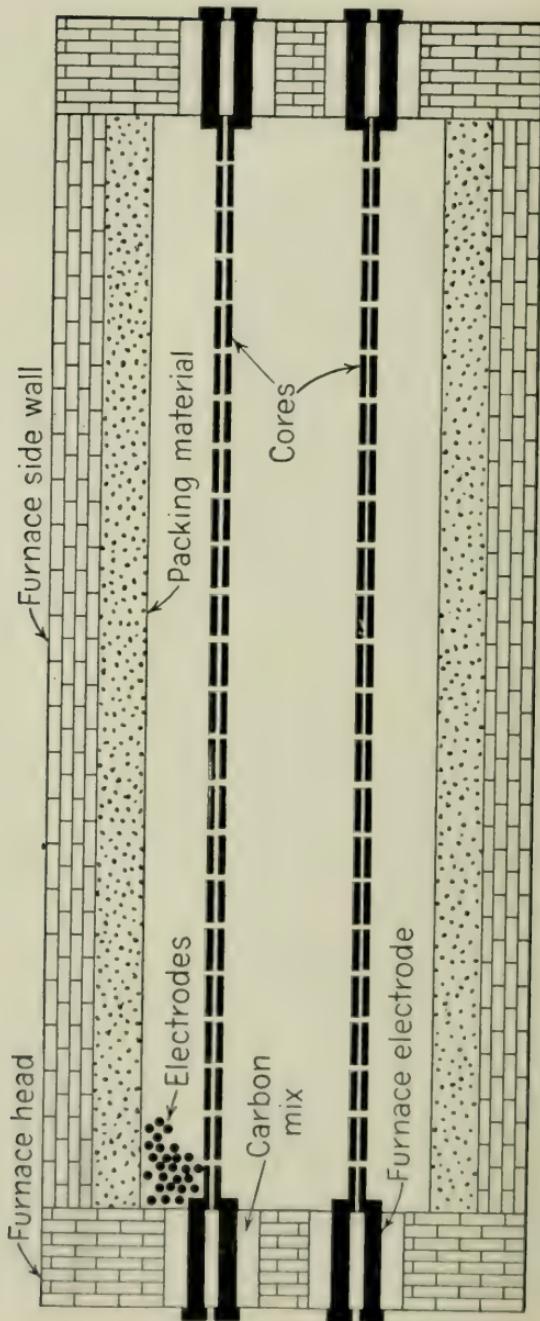


FIG. 69.—PLAN OF ELECTRIC BAKING FURNACE

at one or both sides so that large quantities of electrodes may be run in by trucks or handled by overhead cranes. Finely ground packing dust is then sifted between the individual carbons to fill all voids, and between the outside row and the furnace walls.

After the furnace has been completely loaded, the channel irons strengthening the sidewalls are put in place and connected with the tie rods across the top of the furnace. Just as soon as a transformer is available, the side busbars are put in place. They are supported and held in position by small arms fastened to and extending from the channels. The busbars are insulated at points of contact with the channel irons.

THE BAKING PROCESS

All of the busbars of the furnace being in place, power is turned into the furnace by running the voltage regulator up to its highest point and closing the transformer circuit through the oil switch in the transformer switch room. The transformer switchboard panels are each equipped with an ammeter connected in on the primary side, a voltmeter connected to the secondary side, a power factor meter and an integrating wattmeter. Furnace log sheets are kept.

The core of the furnace, being of much lower resistance to start with, naturally takes most of the current at the beginning of the run. As a result, it heats up at a faster rate. Fig. 70 shows a comparison of the rate of heating of an average core, and the rate of heating of the temperature points. The core curve does not bear out the statement of some electric furnace men that the cores reach a temperature as high as 2,000 deg. C. during the run. The curve seems to agree with the fact that core carbons are seldom found to be graphitized, which would be the case if the core were to reach a temperature of 2,000 deg. C.

The cores, heating up at a more rapid rate, reach final temperature sooner than the rest of the furnace, which is gradually heated by radiation from the core until it conducts of its own accord. From the fact that the resistivity of the

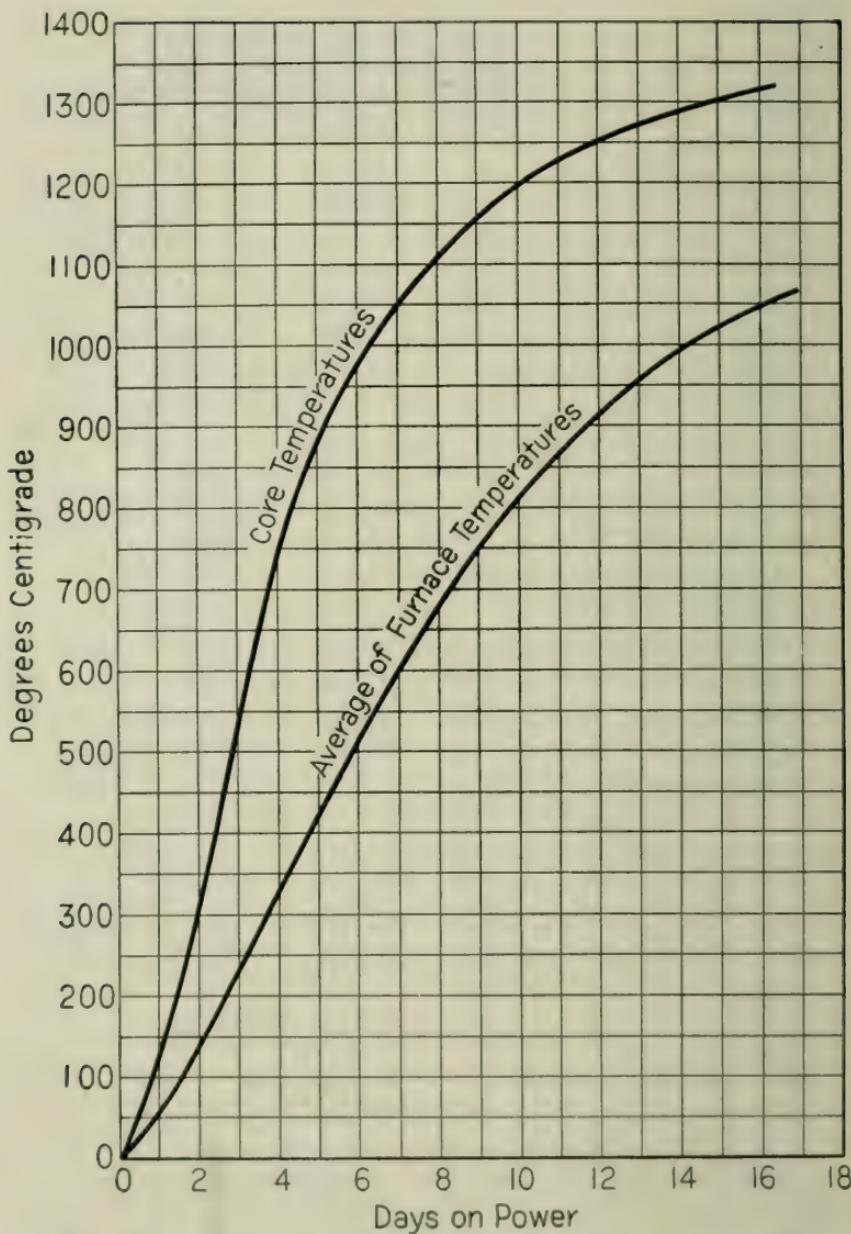


FIG. 70.—COMPARISON OF CORE AND FURNACE TEMPERATURES

carbons just inside the core is lower than that of any other portion of the carbon pile, the indications are that this portion of the carbon pile reaches the highest temperature.

Insulation of the carbon pile depends for its effectiveness upon four things: (1) The condition of the bottom of the furnace, (2) the age of the brick sidewalls, (3) the time the sidewalls have remained intact, and (4) the width of the packing material insulating layer. The bottom becomes soaked with the pitch and tar distilling off from the binder in the electrodes during baking. With an old bottom, considerable heat will be radiated off. In this case the bottom itself ceases to act as an insulator and becomes a conductor. The brick of the sidewalls are also penetrated with tar and pitch fumes, which gradually coke inside and on the surface of the brick, thereby seriously lessening their insulating power.

The packing material which is principally used is pulverized calcined petroleum coke, ground in a mill of the swing hammer type, to pass a 10-mesh screen. This material has almost entirely supplanted magnesia, carborundum and fireclay, which were formerly used as packing materials. Petroleum coke does not adhere to the electrodes, making them difficult to clean, as do magnesia and carborundum. Being of the same material as the electrodes, it does not contaminate their surfaces, and furthermore is easier on the grinding mills.

During baking there is a tendency for the ash of the packing material to fuse as a result of the high temperature. Coming in contact with the sidewalls and bottoms, the packing material becomes more and more contaminated with fireclay and silica with each run. Tarry matters distilling from the electrode binder are "cracked" when they come in contact with the hot packing material on their outward passage. As a result they tend to bind together the packing material particles, and at the end of the run it is necessary to send the packing material to the grinding mills for pulverization before it can be re-used. It leaves the furnace in

the form of a very friable clinker. Practically all of the packing material, save what is lost by oxidation and handling, is recovered at the end of the run.

As soon as the furnace has reached final temperature (1,000 to 1,100 deg. C.), the transformer circuit is opened, the side busbars of the furnace removed and placed on a furnace which is ready to go on power and the transformer circuit is closed. The furnace is then permitted to cool to a sufficiently low temperature to permit of unloading. Of course, it is understood that even if it were feasible to unload the furnace at such a high temperature, the electrodes would oxidize very rapidly and cause a large loss of material. Permitting the furnace to cool before unloading keeps the red hot carbons away from the air and prevents oxidation losses.

After the furnace has cooled, the tie rods across the top of the furnace are removed and the top layer of packing material is shoveled off. The electrodes are still appreciably hot at this time. In order to expedite the process, either one or both sidewalls are torn down. All packing dust is removed for regrinding preparatory to re-use. The electrodes are handled with the aid of tongs, for they are usually too hot to be removed by hand.

With the proper packing material, electrodes will be produced with a fairly clean surface requiring little further work on them. The most desirable baked charge is one that almost unloads itself — that is, the baked electrodes are loosened and removed with little effort. Packing dust grains larger than the No. 10 screen size are liable to sink into the carbons during the plastic stage of baking and be baked in place. This causes an extremely rough carbon to be produced, requiring much surfacing work to be done on it.

An average furnace under good operating conditions and control has approximately the following cycle: Loading (including time for making repairs if any), 2 to 4 days; on power, 12 to 20 days; cooling, 20 days; unloading, 3 to 5 days, giving a minimum cycle of 37, and a maximum of 49 days.

GAS-FIRED BAKING FURNACES

Gas-fired electrode baking furnaces are all built on the "ring" principle — that is, they are in the form of an endless chain of individual units. They are regenerative, without having regenerators. They consist essentially of brick chambers, in which the green electrodes are placed, heated by gas, burning in flues along the ends and sides, and in some cases under the bottom of the chambers.

The gas-fired furnaces may be classified in four different ways: First, in reference to the position the chambers or "pits," as they are termed, occupy in respect to each other which gives us the *longitudinal furnaces*, in which the pits are end to end, and the *latitudinal*, in which the pits are side by side. A second classification, in reference to the baffles in the flues heating the pits, gives the two classes *horizontal* and *vertical baffle furnaces*. A third, in respect to the pits, yields the *continuous* and *non-continuous pit furnaces*. The last classification is in respect to the tops of the chambers, as to whether they are covered or not. This accounts for the two classes *open-* and *closed-top furnaces*.

The general construction will probably be best understood in connection with the drawings of a typical furnace. Fig. 71 shows the plan of an eighteen four-pit-section, longitudinal, non-continuous pit, open-top furnace. The entire furnace forms a rectangular "ring" around the centrally located gas main. The dotted lines show the position of the flues, which are continuous for the entire furnace. The flues for the burned gases, which are usually termed waste-gas flues, are on the outside of the furnace and parallel to the gas main. Oftakes from the gas main and openings into the waste-gas flues are shown by the larger circles. Lines joining the centers of the openings in the gas and waste-gas mains are parallel. Openings into the flues heating the pits are shown by the smaller circles. Connections between the gas main and flues and waste gas and flues are not permanent, but temporary and portable. When not in use, the gas-main, flues and

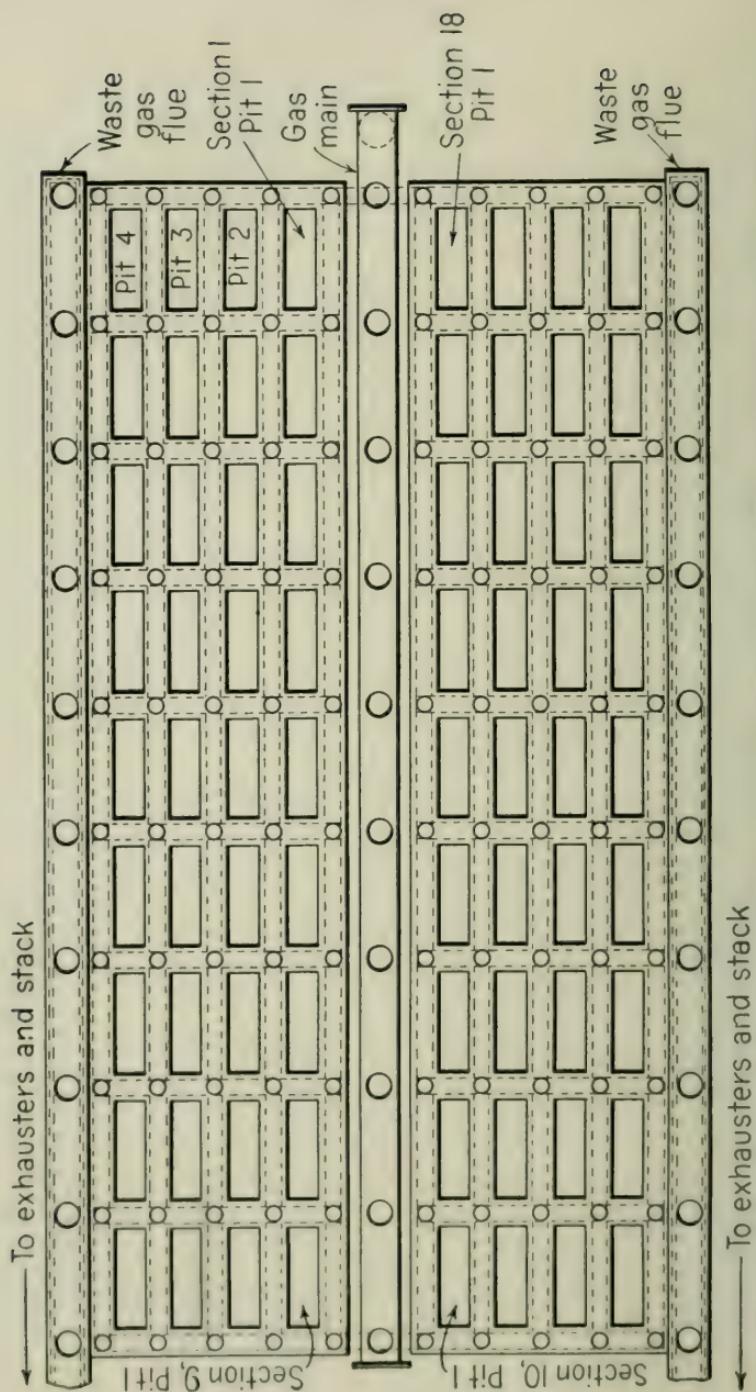


FIG. 71. - PLAN or 18 SECTION LONGITUDINAL PIT TYPE OF GAS FIRED ELECTRODE BAKING FURNACE

waste-gas flue openings are closed by heavy cast-iron covers, fitting in rings or seals so that they can effectively and easily be "luted" with sand or fireclay.

The portion of the furnace located between two gas-main offtakes and the corresponding waste-gas flue entrances is termed a "section." Equalizing flues extend over the width of the section.

Gas mains are usually cylinders of steel plate lined with a highly refractive firebrick. Waste-gas flues are generally built of brick, rectangular in cross-section save for the top, which is closed over by corbelling the brick. However, no brick flue, no matter how well built, is gas tight for any considerable length of time. As a result there is a growing tendency to build waste-gas mains in a manner similar to the central gas main.

The carbon pits are formed by the brick walls of the flues, which are built of tongue-and-groove brick. The ends of the pits are tied in by the use of tongue-and-groove corner brick. All of the brickwork is laid with a refractory bond, being rubbed into place with a minimum of mortar, in order to obtain the tightest joints possible.

The reader has probably inquired of himself by this time, "Where are the gas valves?" There is a slide in the gas main at its entrance to the furnace, but this is used only when operation of the entire unit is started or stopped. There are valves of the bell or gate type in the so-called "gas elephants," which are the portable connections between the gas main and the flues.

Connection between the flue openings and the waste-gas flue is affected by the use of waste-gas elephants, built of steel plate.

In order to cause the burning gases to give up as much of their heat as possible to the section in which they are burning, baffles in the flues are used to lengthen the distance the gas must travel. Two types of baffles are employed, horizontal and vertical. Figs. 72 and 73 show sectional elevations through the middle of flues and illustrate horizontal

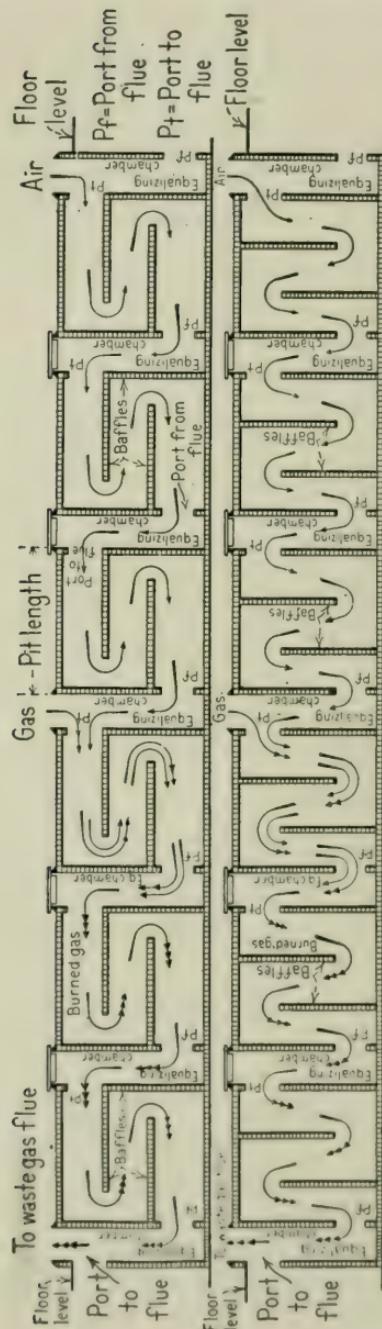


FIG. 72.—(Upper Half) SECTIONAL ELEVATIONS THROUGH MIDDLE OF FLUE SHOWING HORIZONTAL BAFFLES
 FIG. 73.—(Lower Half) SHOWING VERTICAL TYPES OF BAFFLES. ARROWS SHOW FLOW OF AIR, GAS, AND
 WASTE GAS

and vertical types of baffles. In each of these the gases leave the flue of each section at the bottom, pass into the equalizing chambers, and enter the next section's flue at the top.

Figure 74 shows the plan of a latitudinal pit furnace. Flues are shown by the dotted lines. In this case the section and pit are identical. The gases advance from one section to the next by passage under the section. When baffles are used that cause the gas to pass from left to right, then right to left, and from the top to the bottom, an even number of baffles along the sides of the pit requires that there be an even number under the pit in order to bring the gases back alongside the gas main for the following section. In a like manner, an odd number of baffles along the side will call for an odd number. With vertical baffles the gases, passing up and down and from left to right, must then pass from right to left under the pit to come back alongside of the gas main for the next section. As there is but a single flue for each section, no equalizing chambers are needed.

The Isbell-Porter Co., of Newark, N. J., has patented a gas-fired latitudinal pit furnace in which it uses clay cylinder burners spaced along the bottom of the flues between the sections. Gas and air rise through these, burning in chambers above the burners. The gases rise and pass around vertical baffles set parallel to the gas main, one on each side of each burner. As a result, one-half of the gases from each burner pass around the baffles on the right hand side and one-half around the baffle on the left hand side, each meeting the gases from the burners adjacent to the one they came from. Here they burn down, pass under the pit and come up through the burners of the flue of the next section. Fig. 74 shows a plan of this type of furnace and a sectional elevation across the furnace and through the pits. The relative positions of the gas-main, flues, pits and waste-gas flues, and equalizing chambers can be seen. These chambers serve to even up pressures and volumes of gases passing through the flues.

Present practice is to build only open-top furnaces — that is, furnaces in which the tops of the pits are exposed. In the

older type furnaces, covers for the tops were used made of firebrick arches held together by channels and tie rods. The arches were portable and interchangeable for any pit or section. Often the flue system was such that the gas burned

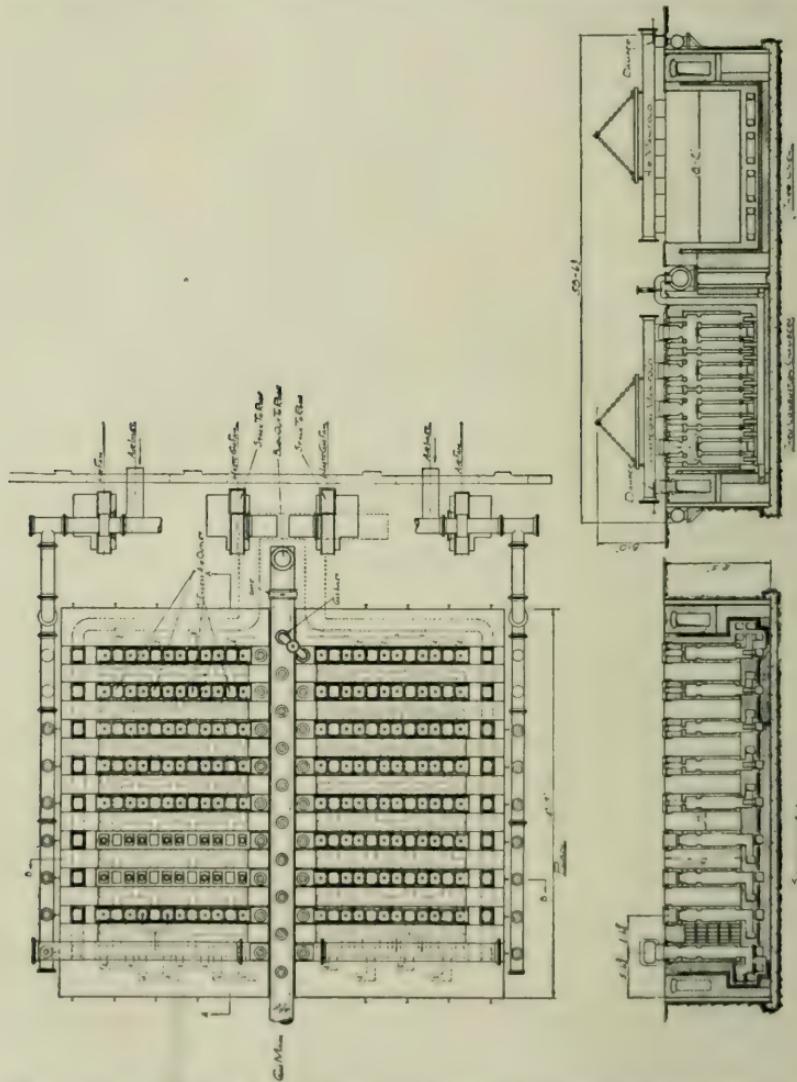


FIG. 74. — PLAN AND ELEVATION OF LATITUDINAL GAS FIRED FURNACE
(Courtesy Isbell-Porter Co.)

over the top of the pit under the arch in addition to burning at the sides and ends. A large number of arch or covered top furnaces have outlived their usefulness, and instead of being rebuilt in the same manner, were replaced by the open-top variety.

The operation of all of the different types of gas furnaces is the same. It is always considered on the basis of an individual section in connection with its preceding and succeeding section. The cycle of operation for each section is: (1) Loading, (2) on waste gas (preliminary heating), (3) on fire (on gas) (heating), (4) on air (cooling) and (5) unloading. For an example, let us suppose that the furnace has been in operation for some time and we find a section ready for loading. It is loaded in a manner similar to the loading of an electric furnace. The carbons are placed on end as closely as possible, with packing dust sifted between them, thermocouples placed in desired positions and a covering of packing material placed over the top layer of carbon. Fig. 75 illustrates the loading of the latitudinal and longitudinal pit types.

It is to be understood that the five operations mentioned in the preceding paragraph are all going on at the same time, but in different portions of the furnace. The section now loaded is ready to go on waste gas. Operation is ordinarily so arranged that a little time allowance is made so that sections can be loaded a short time in advance.

Unloading is accomplished by "stripping" the pit; that is, removing the layer of packing material on top of the carbons. The layers of carbons at the top are "pulled" by means of short-handled tongs and the lower layers by long-handled ones. The pits are normally too hot for workmen to go down in them during unloading. After the carbons are removed and the pits have cooled considerably, the workmen enter and remove the packing dust from the bottom of the pit and any that has been baked in place and is adhering to the side and end walls of the pit.

Figure 76 shows a typical curve of pit temperatures. From

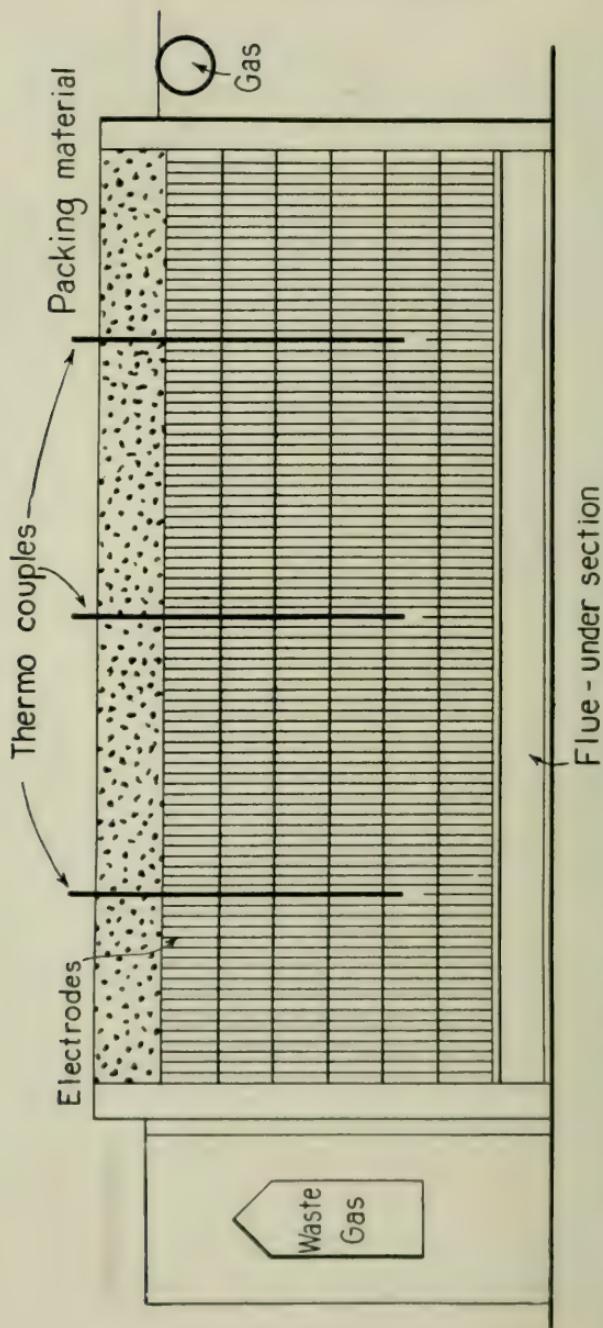


FIG. 75. — ELEVATION OF SECTION OF LONGITUDINAL TYPE OF FURNACE, SHOWING LOCATION OF THERMOCOUPLES

fourteen to eighteen cycles per year are completed per section, with an average of sixteen.

Flame temperatures are generally 200 or 300 degrees

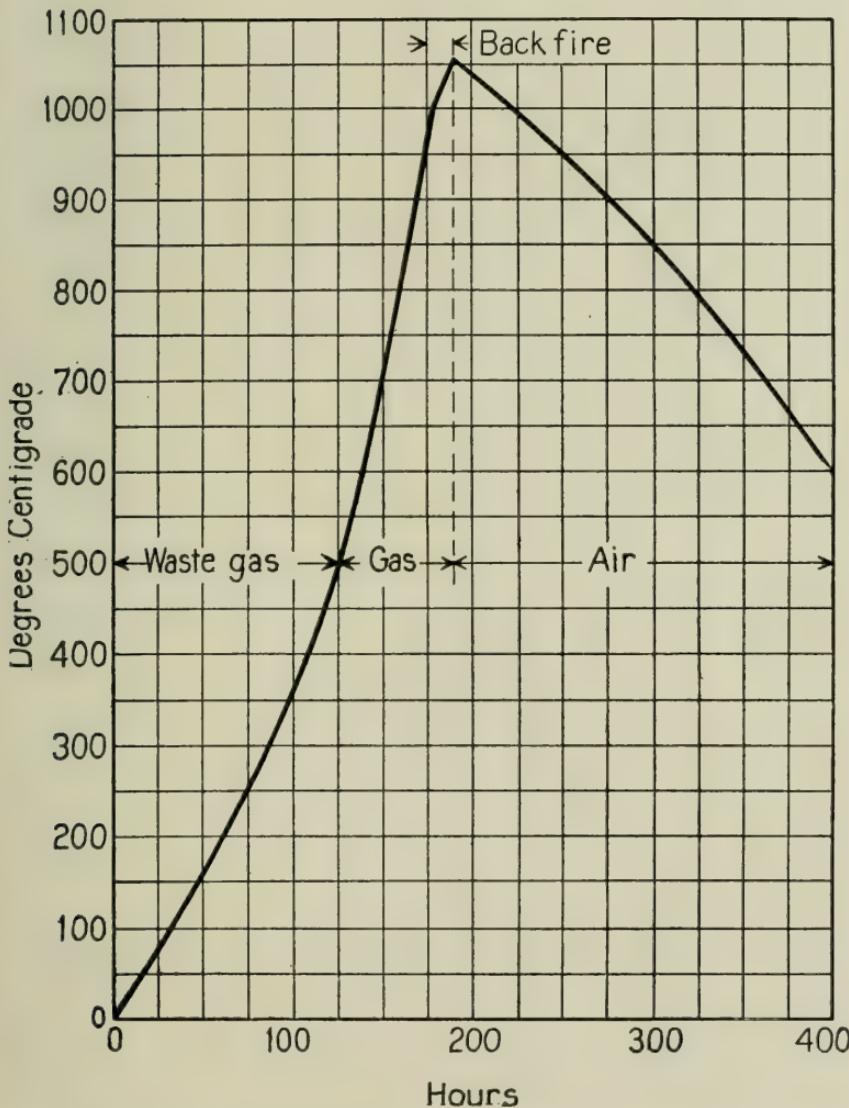


FIG. 76.—BAKING CURVE OF PIT TEMPERATURES IN TYPICAL GAS FIRED FURNACE

higher than the final pit temperatures, and often go as high as 1,400 deg. C. when using well-heated air and hot gas of higher B.t.u. value. Air temperatures at the point where the air meets the gas are between 500 deg. and 600 deg. C. Waste gas temperatures fall to as low as 350 deg. C. at the entrance to the waste-gas main, but are usually 100 or 200 degrees higher than this.

In the design of baking furnaces the term "spacing" is used to refer to the number of furnace sections through which the air must pass during preheating before it meets the incoming gas. This spacing of air and gas depends upon the rate of cooling of the sections on air, the temperature required of the air for combustion and the available suction. The air temperature desired is the highest possible, as the hotter the air the hotter the flame temperature. The greater the spacing the longer will be the distance that the air passes over previously heated sections and the closer the temperature of the air will approximate that of the section next to the one on fire. The longer the air passes through a section the cooler the section will become. Usually, however, the suction available limits the number of sections through which the air can be drawn for preheating. The cycle of operations is lengthened by increased time interval of greater spacing as any given section is on air a longer time.

The spacing of the gas and waste gas is determined by the drop of the waste-gas temperature and the available suction. It is desired to bring the waste-gas temperature to as low a point as possible with a minimum loss of the sensible heat of the waste gas.

From the foregoing description, it can be readily seen that any furnace is not limited to a single fire, but may have many more. In this case we must make allowance for another spacing, that of fire to fire. It must be great enough to allow time for the preparatory operations, loading, unloading and repairs to take place before the cycle of one firing follows the cycle of another. The number of sections to a furnace and pits to a section is theoretically unlimited. The

number of fires is fixed by the number of sections to the furnace and the spacing of the fires.

The fuel used for firing the furnace is generally raw producer gas. The producers in present practice are located as near the furnace as possible so that all of the sensible heat of the raw gas may be utilized. Producers operate on bituminous gas coal, and are of the updraft pressure type.

At first glance at a gas-fired electrode baking furnace, it seems strange that only an extremely small amount of gases, from the distillation and cracking of the green carbon binder, is given off through the uncovered tops of the pits. The walls of the pits are not gas-tight and as the flues are under suction, the pits come under suction through the crevices of the walls. As a result, the vapors and tarry matters arising from the distillation-cracking action of the binder are drawn off into the flues and become a portion of the waste gas. For this reason waste gas is usually of a heavy greenish-yellow color, having a marked deleterious effect on vegetation. In the earlier stages of the industry, when electrode plants were located at places sparsely populated, this condition was not important. With increases in population, the necessity of eliminating the nuisance of the waste gas became apparent. Electrode works started to scrub waste gas and to recover, as a product of the scrubbers, a thin liquid tar.

Control on the furnaces is obtained by regulation of the cross-section of the air openings, by regulation of the gas-elephant valves, and waste-gas valves or "dampers." Additional control on individual sections is obtained by regulation of the ports from and to the flues in the equalizing chambers.

As gas-fired ring furnaces for electrode baking have not as yet been definitely standardized, their design involves a considerable amount of cut-and-try procedure. The entire field of gas baking, however, is a promising one, and the possibilities of its development are relatively great.

In general the length of the pit will have to be a multiple of the average electrode diameter. The waste-gas flue must

be large enough to take care of all products of combustion, plus excess air, plus the vapors distilled and cracked from the electrode binders. Allowance must be made in designing the waste-gas flues to take care of the products of the maximum number of fires possible on each side of the furnace. The latest furnaces built have been of the longitudinal pit, vertical baffle, open-top variety. Vertical baffles, with openings through the top of the flues, permit the possibility of cleaning the flues by blowing them out with compressed air or sucking out dust, pieces of brick or mortar, etc. Horizontal baffles do not permit this.

In the design of the flues (and equalizing chambers if any) such combinations must be used as will give as intimate a mixture of the air and gas particles as possible, for the better this mixture the better will the gas be burned and the greater the heating power obtained from the gas. Having the gas and air come from opposite directions, meeting, and continuing at right angles to their previous flow, provides a good and intimate mixture.

A comparison of gas and electric baking shows that both types have low thermal efficiencies.¹⁶ The cost of a unit of energy obtained from electrical sources is much greater than that obtained from the gasification of coal and the combustion of the resulting gas. Although the electric unit is ten times as large as the gas section unit, the yearly production of the electric unit is not more than one and a fourth times that of the gas unit. This is because of the greater number of cycles possible with the gas furnace. In the electric furnaces there is no heat recovery of any sort, while in the gas unit the heat of the waste gas and baked electrodes are both partly recovered.

The greater ease and closeness of control of the gas-type furnace is a decided advantage over the electric. The gas type permits the more or less valuable products of electrode

¹⁶ The heat necessary to raise the material to the required temperature (calculated from the specific heat of the material) divided by the actual heat used; See Richards, "Metallurgical Calculations."

baking to be recovered. In the electric type all sensible heat of the finished baked electrodes is entirely lost, while in the gas type it is almost entirely recovered and used to give preliminary heating to the other materials. The maximum temperatures are much greater in the case of the electric type than in the case of the gas type, and the latter is limited by the softening point of the furnace brickwork and the possible air temperatures obtainable. Both types use about the same amount of absolute energy in baking and a large part of the difference in cost may be shown to be due to the fact that a heat unit from gasified coal is much cheaper than one from electric power. The average life of an electric furnace is about three or four times that of a gas furnace.

Finished electrodes from electric furnaces are more difficult to clean than from gas-fired ovens, but the electric baked have the advantage of having a somewhat lower resistivity. Packing dust after being used in electric furnaces is more difficult to grind and prepare for re-use than is the case with the dust from gas-fired units where fusing temperatures for the ash of the packing material has not been reached. Electric furnaces are generally very dirty, as the products of baking burn on the outside of the furnace. Gas-fired units, on the other hand, have the baking products drawn off in the stack along with the waste gases and as a result properly operated gas units are comparatively clean.

CLEANING, TESTING, MACHINING AND SHIPPING

Up to this point, the discussion of carbon-electrode manufacture has been carried through the baking process. The green electrodes, which are made of a combination of carbonaceous materials, the properties and qualities of which vary widely with temperature changes and which have a high electrical resistance and a low tensile strength, have now been changed into baked electrodes, consisting of material with uniform properties over a wide temperature range and with lower electrical resistance and higher tensile strength than the green electrode.

The electrodes as they come from the baking furnaces are dirty — that is, they have adhering to their surfaces some of the packing material in which they were baked. In the case of carbons with which a correctly graded packing material was used, most of the packing dust can be easily removed by knocking or brushing. Sometimes, however, cases of carelessness occur when use has been made of a low fusing packing dust, high in ash content. As a result, large lumps of packing material are attached to the surfaces of the carbons and are removed only with difficulty. At other times sufficient care may not have been taken in placing packing between all of the surfaces of the carbons when loading the furnace. The result is that when the carbons are softened in the early stages of baking, they become welded together and when baked in this manner give malformed electrodes. These, of course, go to the scrap pile.

Methods of cleaning differ according to the shape of the finished electrode. They may be divided into three general methods — (1) brushing, (2) stoning and (3) tumbling. Although the method used depends primarily upon the shape or form of the finished electrode, the amount of packing material to be removed must be adjudged a factor of secondary importance. Plates, of course, could not be tumbled in a tumbling barrel without an excessive breakage loss. The same holds true for long, small-diameter electrodes. Electrodes with square or rectangular cross-section cannot be tumbled, as their edges would be rounded off as a result of the process.

Usually two or all three methods are employed in conjunction with one another. Carbons as they come from the furnace are sent to some sort of power-driven brush with steel wire bristles. Plates can be cleaned quickly with a pair of brushes somewhat wider than the width of the largest plate, mounted horizontally and rotating in opposite directions. The plates are cleaned by passing them between the brushes. Square and rectangular shapes are often brushed on a similar type of machine, but in which the brushes are

mounted vertically and the carbon passed through twice, or through two successive machines, being given a quarter turn in the plane of its cross-section between the first and second brushings so that all sides may be cleaned. Round electrodes are often cleaned on the periphery of horizontal or vertical wheels, and in some cases by steel brushes mounted on the inside of revolving rings.

Carbons which cannot be completely cleaned on the brushes are finished on the stoning wheels. These are large wide-faced wheels of emery or other similar abrasive material. Small round electrodes whose length does not exceed more than six times their diameter can be very successfully and readily cleaned by tumbling in steel tumbling barrels loaded about seven-eighths full. Cast-iron, star-shaped jacks (about $3/4$ to 1 in., size) are used to assist in the cleaning operation. The tumblers are horizontal steel cylinders with removable covers, for loading and unloading, mounted on hollow shafts connected to each end. One end is open to the air through the hollow shaft, and the other is connected to piping leading to the exhauster of a dust-collecting system which discharges into some sort of collector, often of the cyclone type. Electrodes which have not been sufficiently cleaned by tumbling go to the brushes and stones for final cleaning.

Cleaning practice in the various electrode plants differs materially even when the same type and size of product are being handled. In the case of small electrodes it was formerly the practice to brush all electrodes, and tumbling barrels were used to clean only those which were too dirty for the brushes. In some modern plants, as a result of scientific management, this procedure has now been completely reversed and considerable saving effected. All electrodes are tumbled for a short while and only those still unclean after this procedure are brushed and stoned. Records of this method with small round electrodes show that all but a small percentage are cleaned without brushing.

It is general practice to equip all cleaning apparatus with

suction hoods, connected to a dust collector. This is done with the view of supplying better working conditions, and also to recover as much as possible of the packing material removed from the carbons.

Mention has been made previously of the resistivity of the carbon electrode. Its discussion, however, has been delayed to this point, since its determination is usually made in the plant testing laboratory, which is generally located in or near the cleaning and shipping departments. In general two methods of testing are used:

1. Measurement is made of the voltage drop, with a given current, through a known distance of an electrode having a uniform cross-section. Direct current is passed through the whole electrode. Resistivity or specific electrical resistance is then obtained by the use of Ohm's law and the formula for specific, calculated from total, resistance. The formula ¹⁷ $\rho = SE \div IL$ gives a result in ohms per inch cube when S and L are expressed in square and linear inches respectively, or per centimeter cube when S and L are expressed in square and linear centimeters.

For ordinary purposes it is sufficient to measure resistance to 0.0001 ohm, a precision of about 5 per cent. By this method the voltmeter will show a voltage drop due to resistance through the whole potential circuit — that is, it will include voltage drop due to resistance of the potential contacts and the lead wires. The resistance of the potential contacts may be practically eliminated by drilling small mercury cups in the carbon or pressing the contact pins against the carbon at a pressure of about 3,000 lb. to the square inch when using a millivoltmeter having a resistance of 1.07 ohms.

2. Measurement is made directly of the resistance of an electrode or a portion of an electrode by comparing it with a standardized resistance by means of a resistance bridge. This method is more accurate than the first, because it

¹⁷ ρ = specific resistance, S = cross-section, E = voltage drop, I = current in amperes and L = length or distance.

is a zero method and comparison is made directly with a standardized resistance the accuracy of which can be made very high. The instrument generally used is the Leeds & Northrup Kelvin double bridge ohmmeter.

Resistivity is calculated from the formula $\rho = (S \div L)R$ where R = scale reading of resistance.

Where measurement is made of the circumference in

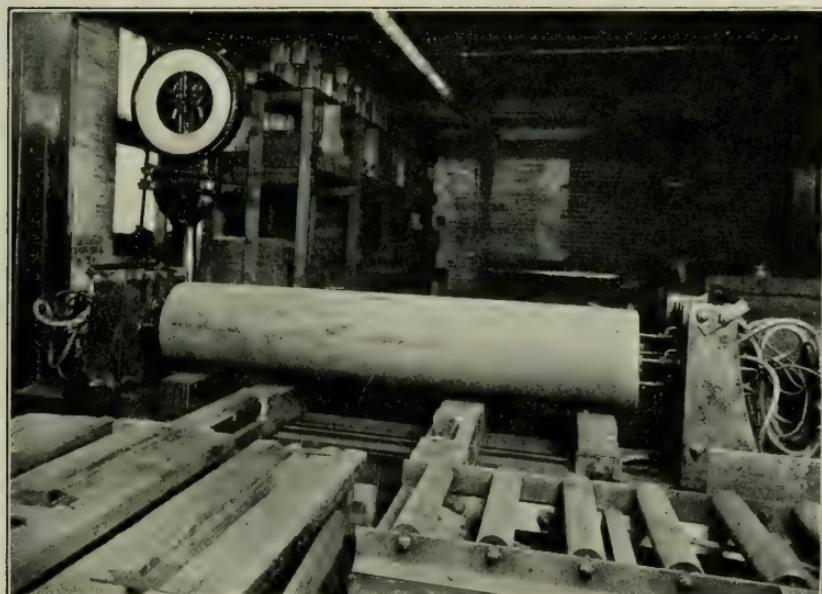


FIG. 77.—COMMERCIAL SET UP FOR THE MEASUREMENT OF RESISTIVITY OF A LARGE ELECTRODE

(Courtesy Acheson Graphite Co.)

the case of round electrodes, this formula becomes $\rho = \text{cir} R \div 12.57 L$.

In plants where large numbers of the same sized electrodes are being made and tested, it is usual practice to provide permanent potential and current contacts. Potential contacts are often V-shaped, made of copper, brass or steel, with knife edges on the inside of the V. While making the measurement, the electrode is supported in a horizontal position

by the knife edges. The pressure of the weight of the electrode against the knife edges of the V is sufficient to afford good contact. Current contacts are often copper, brass or steel plates in which there are imbedded short cylindrical rods, pointed at the ends. The points of the rods are pressed

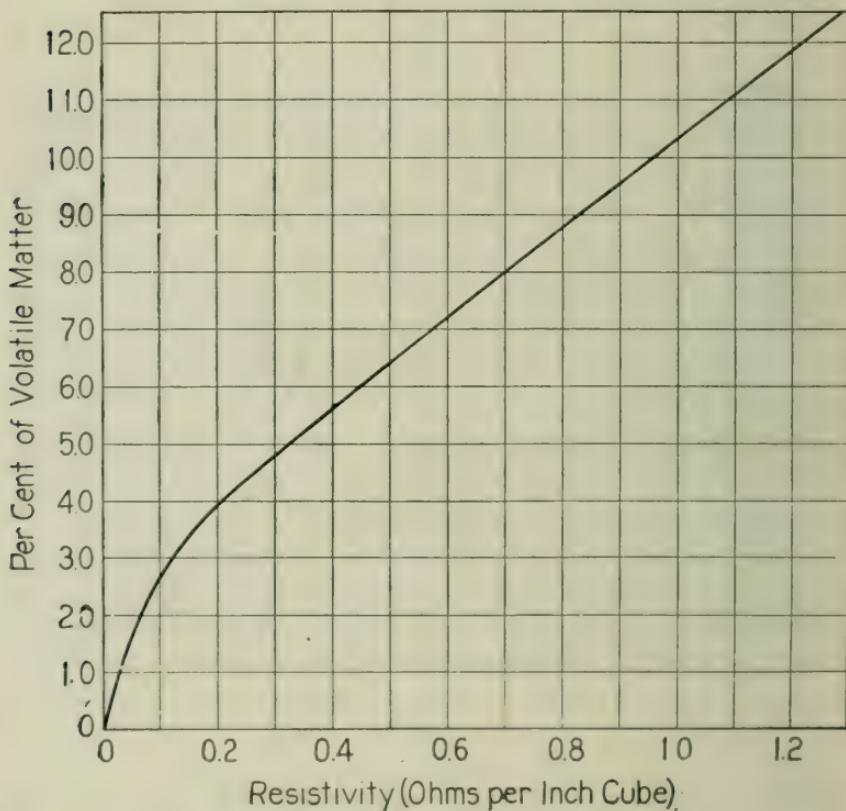


FIG. 78.—RESISTIVITY-VOLATILE MATTER RELATION OF CARBON ELECTRODES

against and into the ends of the electrode by pressure exerted against the plates in which the rods are imbedded.

The electrical resistivity of carbon electrodes varies inversely as the elemental carbon content, directly with the ash content, directly with the percentage of volatile matter

and inversely as the apparent and real densities. As the percentage of elemental carbon increases, the percentage of ash and volatile matter will decrease and the resistivity will decrease. As the percentage of ash increases, there will be more and more of materials whose known resistances are greater than that of carbon, and the resistivity of the material as a whole will increase.

The curve in Fig. 78 shows the resistivity-volatile matter relation of carbon electrodes. The relation between real density of electrodes and resistivity is shown in Fig. 79.

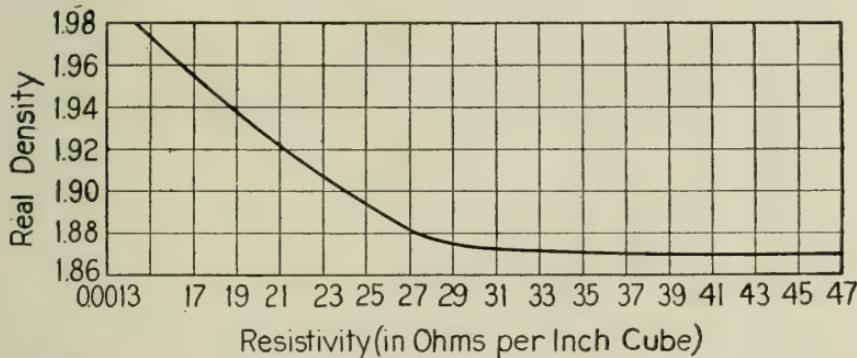


FIG. 79.—RESISTIVITY-REAL DENSITY CURVE FOR CARBON ELECTRODES

Resistivity increases with decreases in apparent density; and as a result, increases with increases of porosity. As the percentage of graphite in electrodes increases, the resistivity will decrease, since graphite has a resistivity of about one-fourth that of amorphous carbon. The real density of an electrode is the density of the material of which it is composed, free from pores or voids. It may be considered as a measure of the chemical composition of the material and increases as the amount of hydrogen in the hydrocarbons in the electrode decreases. It is thus an indication of the relative rate of oxidation of the electrode, it being a general rule that hydrocarbons high in hydrogen are most readily oxidized.

The apparent density — that is, the density of the carbon

including the pores or voids — may be considered as a characteristic of the mechanical structure. It is influenced by every process through which the carbon goes in the manufacture of the electrode and is in general a measure of the relative rate of disintegration of the electrode in use. For large electrodes the most satisfactory method is to weigh the whole electrode and calculate its volume from its dimensions. Where W equals weight and V volume, then

$$\frac{W \text{ (in lb.)}}{V \text{ (in cu. in.)}} = \text{A.D. (apparent density) in lb. per cu. in.}$$

or commonly

$$\frac{W \text{ (in grams)}}{V \text{ (in c.c.)}} = \text{A.D. in grams per c.c.}$$

To obtain a precision of 2 per cent, the weight and length should be measured to 1 per cent and the diameter or periphery to 0.5 per cent.

The cleaned carbons are inspected for cracks, flaws, shape, surface roughness and uniform hardness throughout the length of the electrode. Cross checks, splits and die rings, discussed previously in reference to the green carbon, may have been developed during the baking process either as a result of defects which slipped by the green inspection or originated in the banking furnace. Misshapen electrodes go into the scrap pile. Occasionally the furnaces may produce electrodes which are perfect except for an end which is so soft that it can be cut off with a knife or easily knocked off. Such carbons are rejected. Unusually rough-surfaced carbons, resulting from a blistered or rough condition in the green or from adhering packing material which has become a portion of the electrode and cannot be removed, are thrown out. All scrap resulting from the inspection of cleaned electrodes is returned to the manufacturing process by being used as calcined material in the grinding and pulverizing mills.

It is at this point, along with physical inspection, that

electrodes are rejected for resistivity above the standard and apparent density below the standard. Carbons of high resistivity are termed "re-bakes" and are returned to the furnaces to be again submitted to the baking process. Electrodes very much below the standard for apparent density because of excessive porosity are thrown into the scrap pile, to go back into process as unground calcined material.

Modern electric steel furnaces are becoming higher powered. The I^2R electrode losses then become of extreme importance. Consequently electrode manufacturers are endeavoring to bring electrode resistivity to as low a figure as possible. Sulphur contamination of electric steel by sulphur from the electrodes has caused the development of electrodes of greater purity, made from selected low sulphur coals and petroleum cokes.

MACHINING ELECTRODES

Cleaned carbons, after passing inspection, are sent directly to the shipping room if they are to be used in their present form. If they are to be threaded or tapped, they are sent to the threading or machining departments.

Good amorphous electrodes are comparatively hard and more or less difficult to machine. High-grade machine-steel working tools are required and the threads are cut, holes drilled and tapped in the same manner that a piece of metal might be worked. Amorphous electrodes have a marked abrasive effect on the tools used in machining them — a fact which necessitates frequent regrinding and replacement. It is the opinion of the author, however, that the comparative difficulty of machining amorphous electrodes has been somewhat overstressed and made to seem more difficult than it really is.

Fig. 80 shows the threading and inspection departments of the Niagara Works of the National Carbon Co.

Furnace manufacturers are eliminating electrode designs which necessitate shut downs for electrode changes. Continuous feed of electrode has become standard practice.

There are two methods by which electrodes may be joined. In the first, both ends are drilled and tapped so that a small threaded plug, or dowel pin, of electrode material may be screwed in the end of one electrode and the adjacent end of the next one. This method of joining electrodes is now the only one used for large electrodes. In the case of small electrodes, it was formerly replaced by one in which one end

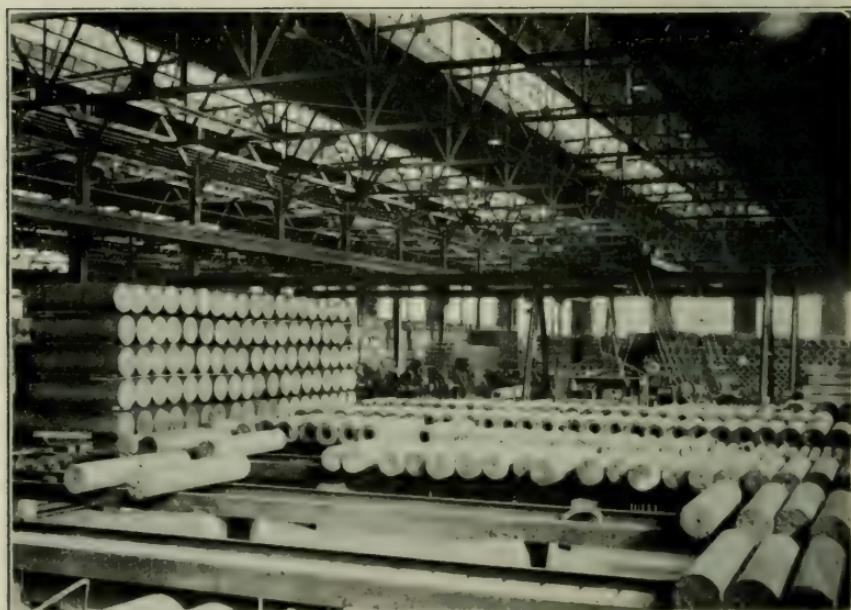


FIG. 80.—THREADING AND INSPECTION DEPARTMENTS, NIAGARA WORKS, NATIONAL CARBON CO.

of the electrode is threaded, and the other drilled and tapped so that the end of one electrode can be screwed directly into the end of another. The first method will be better understood by referring to the illustration of electrodes joined for continuous feed as shown in Fig. 81. The illustration shows the method of assembly.

The molded dowel pin, made into its final form in a single pressing operation in the "green" and then baked, is no

longer widely used. The molded dowel pins were satisfactory as far as high apparent density and strength were concerned. However, the threads were molded in the electrodes



FIG. 81.—JOINING ELECTRODES
(Courtesy National Carbon Co.)

as well as the threads on the pins. Because of shrinkage and expansion in the electrode in forming and baking, the clearances were large and the threaded holes not always centered. These defects resulted in the edge of one electrode often over-

hanging the edge of the other so much that holder trouble was experienced frequently and a broken holder resulted. In addition the large clearance made it possible for the stresses in the connecting pin to be accentuated since the pins were not always in straight tension.

Present day dowel pins are turned out of electrodes large enough so that the dowel pin diameter is approximately half the electrode diameter. Electrodes are now drilled and threaded in special self centering lathes whose bearings are protected from the abrasive carbon dust. Mechanical details on the dowel pins, such as an end boss, champering the first thread, reduction of thread tolerances, have done away with electrode overhangs. Joint trouble has been reduced to a minimum.

American graphite manufacturers have discarded the joining of electrodes whereby one end is threaded and the other drilled and tapped. This method has been replaced entirely by the nipple or dowel pin joint, even for electrodes as small as $1\frac{1}{4}$ " in diameter. Graphite electrodes, due to the accuracy to which they can be machined, require no joint paste.

The desirability of using joined electrodes in any process is mainly a matter of calculation; the cost of power, the cost of electrodes and their length will decide the question. Offsetting the many advantages of continuous or joined electrodes are these disadvantages: (1) Machining operation (drilling, threading and tapping) increase the cost of the electrode. (2) The contact resistance between the portions of a built-up electrode causes loss of energy. (3) The joint is apt to loosen and to increase these energy losses, or the end of the electrode in the furnace may drop off, causing short circuits or other troubles.

On the other hand, the joint in a built-up electrode length serves as a very good thermal valve and lowers the thermal conductivity of the electrode, lessening the amount of heat conducted out through the electrode from the furnace.

In cases in which the furnace and the electrode holder

permit the use of the electrode down to a small butt, in many cases it will be found more advisable not to join the electrode.

A good electrode paste is always used in practice to cut down the joint resistance losses. Experiment has shown that this joint resistance decreases as the electrode heats up and the paste dries or bakes. With the well-made electrodes the joint resistance, expressed in equivalent electrode length resistance, is very small.

The electrode manufacturers put up electrode pastes ready for use. They are usually thick suspensions of pulverized carbon or graphite in some medium that will be quickly volatilized by the heat at which the electrode is used. The chief difficulty with pastes is that precautions must be taken to prevent their drying out and hardening, after which they are almost useless.¹⁸

SHIPPING

After machining, the electrodes are inspected, those at fault returned to be re-machined if the fault can be corrected, or if not, are sent to the scrap pile to be used in the process as unground calcined material. The next step in process is shipping the finished product.

When a through shipment can be made, electrodes in carload lots are carefully packed and braced in the car without being boxed. In less than carload lots, it is usual practice to employ wooden boxes, the sizes of which vary according to the size of the electrodes. Sawdust is used to hold the carbons in place and prevent breakage. In the case of amorphous carbons, case sizes and weights will vary with electrode sizes.

The requirements of the trade for both graphite and amorphous carbon electrodes vary between very wide limits. For this reason, the different electrode companies make no attempt to carry in stock all of the various sizes and shapes.

¹⁸ For a very comprehensive discussion of the various methods of joining electrodes, the reader is referred to *Stahl und Eisen* for March 20 and April 3, 1913, translated into English in *Chem. & Met. Eng.*, June 1913, p. 321.

Carbon electrodes are manufactured in any size and shape desired. For ordinary use, the cylindrical or square shapes satisfy all requirements.

The tendency in the industry is to make larger and larger



FIG. 82.—THE 20-INCH ELECTRODE, THE LARGEST PRODUCED IN 1922

(Courtesy National Carbon Co.)

electrodes to satisfy the requirements of electric furnaces, the dimensions and capacities of which are ever increasing. In 1922 the largest single electrode made, as shown in Fig. 82, was 20" in diameter, 180" long, and weighed 3,180



FIG. 83.—THE 40-INCH ELECTRODE OF TODAY
(Courtesy Chemical & Metallurgical Engineering)

pounds. The largest single electrode which the industry has produced was made recently by the National Carbon Co. It is 40" in diameter, 110" long and weighs approximately 8,000 pounds. This electrode is shown in Fig. 83. The difficulties involved in its manufacture can only be appreciated by those who have endeavored to make electrodes.

If the demand existed, this company is equipped to make electrodes up to 45" in diameter. Certainly, it is a long cry from Bunsen's first little sticks of carbonized wood to the mammoth high-density electrode of the present day! Bunsen's electrodes would float on water; the modern electrode has a density more than 1½ times that of water.

At the present time practically all the anthracite used in electrothermal electrodes is electrically calcined. Commercial carbide, ferro alloy and electric steel furnaces are increasing in size; larger electrodes are called for as well as electrodes which allow a greater current input into the furnace. Electrothermal electrodes of lower resistance, which allow the use of higher current densities, are now produced to meet this demand. The tendency is for greater diameter electrodes; the present 40" diameter will soon be surpassed by the promised 45".

ECONOMIES AND ECONOMICS

The complete flow sheet of electrode manufacture is introduced at this point to complete the discussion of processes. (See Fig. 84.) A glance will show that the industry loses practically nothing as waste and produces no byproducts. Green electrode scrap is re-used in process, gases from calcination are burned to heat the retorts to calcine additional material. Wherever possible, dust recoveries are made. Tar produced in the industry is used again as a binder; even producer gas soot from the soot legs is used as packing material. Recuperative and regenerative heating systems are the foundation of the present-day calcining retorts and baking furnaces. Scrap from the cleaning departments is re-used as unground calcined material; adhering packing material is recovered and carried back into process. The unconsumed portions of finished electrodes are sometimes used as raw materials. The circle is complete and endless.

Graphite electrodes cost two to two and a half times as much per pound or per piece as corresponding amorphous carbons. This might be explained by the fact that elec-

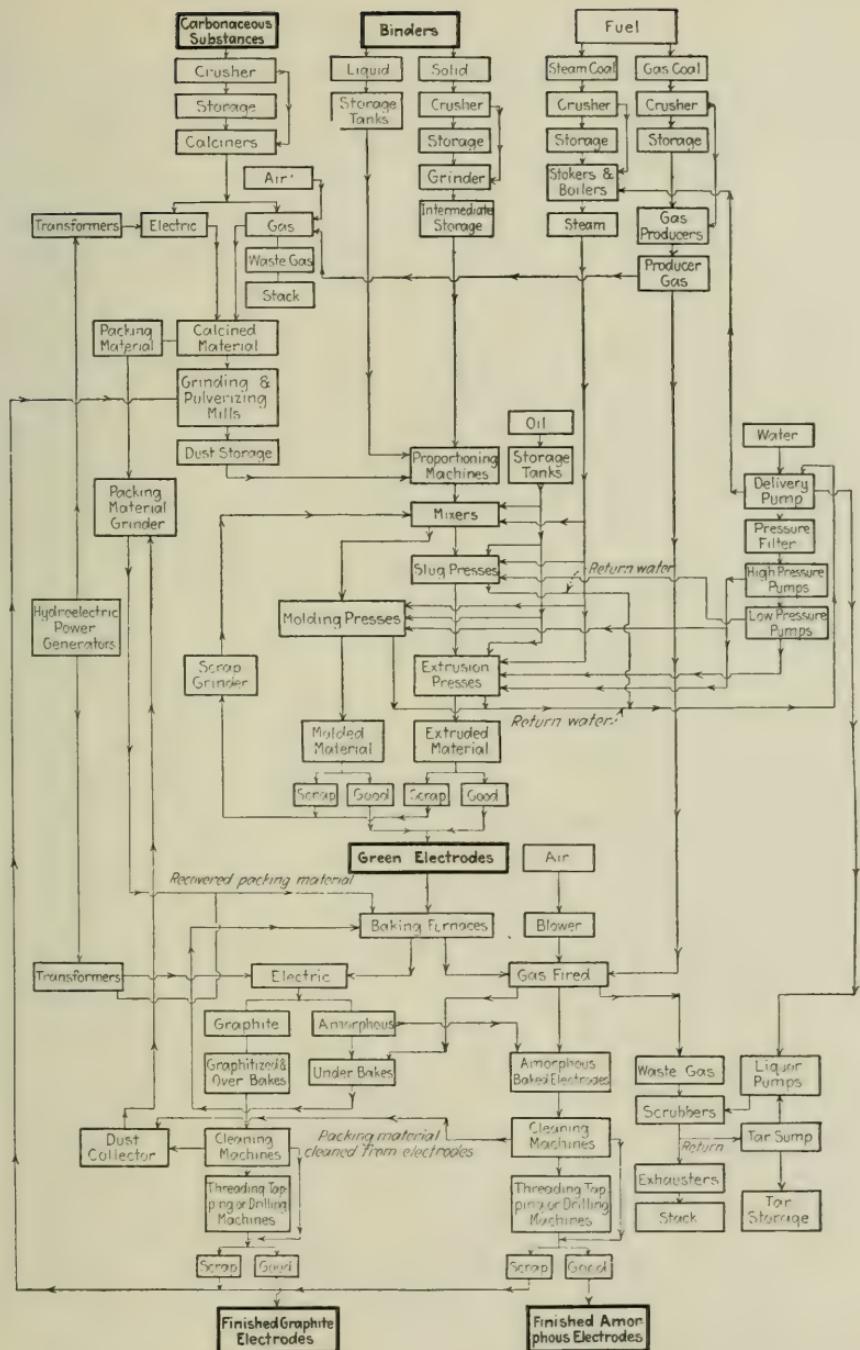


FIG. 84.—FLOW SHEET OF CARBON ELECTRODE MANUFACTURE

trodes to be graphitized cannot be baked in gas-fired furnaces, which, it will be recalled, has been shown to be far cheaper than the electric method. In the second place, in order to graphitize a carbon article, several times as much power is used as would be needed to convert it into a good grade of amorphous carbon. By far the largest cost item in graphite electrode manufacture is the baking to graphitization.

The cost of any particular size of electrode to the trade will depend upon several factors: (1) The difficulty of forming that particular shape in the green. (2) The percentage of scrap normally resulting and necessary to reprocess. (3) The difficulty or ease of loading, baking and cleaning the particular shape and size. (4) The percentage of breakage, replacement and excess necessary to complete the order. In the case of both graphite and amorphous carbons the percentage of breakage during and after baking is a serious item.

A comparison of the two forms of carbon of which electrodes are made, amorphous and graphitic, is given in Table XXIX. Good graphitic electrodes have about one-fourth the resistance of good amorphous electrodes of the same size. The apparent density of graphite electrodes is usually two or three points higher than that of fine-grained petroleum coke electrodes. The tensile strength of amorphous carbons is about 50 per cent greater than that of graphitic carbons of the same diameter. It will be found that ordinarily graphite electrodes are much purer — that is, have a lower ash — inasmuch as almost all of the metallic and metalloid oxides were volatilized by the temperatures reached during the baking to graphitization. Copper, aluminum and iron are included in the table to permit of a comparison with carbon electric conductors. Graphite and amorphous carbon electrodes are not competitors. The properties of each particularly fit it for distinctly different fields. The field of the amorphous carbon, used in large quantities, is that of electro-thermal work, where the fact that its cost is only one-half to one-third that of graphite offsets any advantages graphite

TABLE XXIX

COMPARISON OF AMORPHOUS AND GRAPHITIC CARBON ELECTRODES

	<i>Acheson Graphite Electrodes</i>	<i>Amorphous Carbon Electrodes*</i>	<i>Gas-baked Amorphous Carbon Elec- trode†</i>	<i>Large Elec- trothermal Electrodes</i>	<i>Copper</i>	<i>Aluminum</i>	<i>Iron</i>
Specific resistance (ohms per inch cube).....	0.00032	0.00124	0.00161	0.00220	0.000065	0.0000120	0.00000380
Specific resistance (ohms per cm. cube).....	0.000813	0.00325	0.00400	0.00550
Comparative section area for same voltage drop.....	1.	3.8	4.4	6.8
Weight, lb. per cu. in.	0.0574	0.0564	0.0560	0.058	0.320	0.090	0.280
Weight, lb. per cu. ft.	99.0	97.5	97.0	100.0	55+	155	484
Apparent density, grams per c.c.	1.585	1.558	1.55	1.60
Tensile strength, lb. per sq. in.	29,000-39,000	24,000-30,000	30,000-50,000
Lengthwise.....	800-1,000	1,000-1,500	1,000-1,500
Crosswise.....	500-600	600-900	600-900
Temperature of oxidation in air, deg. C.	640	500	500	500	500

* Very good electric baked electrode (small).

† Typical small electrode.

might have. The particular field of graphite is that of electrolytic work, where its low resistance and long life are very important. Graphite electrodes are extensively used in the electrolytic production of chlorine and caustic, the chlorination of gold ores, the recovery of copper, nickel and zinc, the production of hypochlorites and many other similar applications.

At the present time most of the carbon electrodes now manufactured are used in electrothermal work. In the United States, graphite has gained a well-deserved distinction for electrolytic work. In Europe, because of many adverse conditions, amorphous carbon electrodes were formerly used in electrolytic work to a considerable extent. Today, however, except for one relatively small installation in England where pieces of retort carbon are still used as anodes, there is no electrolytic installation in Europe that is not using graphite anodes. The use of both retort carbon and platinum has practically entirely disappeared. Despite advances by European makers, Acheson graphite is still superior, to judge from the statement of European consumers of the product.

For electrolytic work a low resistivity is both desirable and essential. In this case, low voltages and high amperages are used per cell. The higher the resistance of the electrodes the greater the voltage that must be applied to the cell and the higher the dead cost of electrolysis. With large currents even slight increases in resistance prove costly.

The apparent and real densities are both of importance. The first gives an idea of the porosity of the electrode, which to a certain extent is an advantage, inasmuch as it increases the active surface of the electrode, but if in excess, the bath liquid will enter the pores and cause a rapid generation of gas, which would tend to break off small chips, especially at the less porous edges. This would mechanically shorten the life of the electrode. An apparent density lower than 1.54 is undesirable, although from 1.4 to 1.6 is used.

Electrodes for electrolysis should not have more than

2.5 per cent of ash, and 4 to 5 per cent, as often found on the Continent, is distinctly disadvantageous. Higher ash content invariably means higher resistivity, with resulting electrical losses. The life of the electrode will suffer in consequence of the higher ash percentage.

In electrolytic work the electrodes are not consumed chemically or oxidized by surrounding air, but are eventually displaced through wear and tear. Impurities in the electrode do not therefore get into the cells in any great quantity through consumption of the electrode. In electrothermal work, however, the electrode is consumed largely by oxidation. The higher the apparent density the greater will be the amount of material packed in a given volume and the greater will be the length of time necessary to consume that volume. A carbon with a low apparent density offers a greater surface for oxidation per unit of weight than one with a high apparent density.

In summing up the requirements, it may be said that the following properties are necessary for the satisfactory performance of an electrothermal electrode:¹⁹ (1) High electrical conductivity (low resistance). (2) Slow rate of oxidation (high apparent density). (3) Great mechanical strengths (particles well bonded together, suitable aggregate and thoroughly mixed). (4) Good shape and accuracy of dimensions. (5) Precise machining. (6) Low heat conductivity.

The Niagara Falls works of the National Carbon Co. was built in 1911. At the 1914 meeting of the American Electrochemical Society at Niagara Falls, that company exhibited a carbon 20 in. in diameter, 84 in. long and weighing 1,450 lbs. In 1927 the same company produced electrodes of 40 in. diameter and 110 in. long, and 30 in. diameter by 180 in. long. Such has been the progress in the United States inside of less than 20 years.

¹⁹ Electrothermal electrode specifications may be found in "The Carbon Electrode," p. 34, published by the National Carbon Co., and "Operating Details of Electric Furnaces," by E. T. Moore, *Chem. & Met. Eng.*, vol. 24, No. 4, pp. 171-6, Jan. 26, 1921.

While there have been many developments in the electrode industry in the past 20 years, the coming decade should bring forth even greater progress. It is possible here only to hint at some of the lines of development along which this progress will be made. Pitch coke is being developed as a raw material as a result of the possible shortage of petroleum coke. Probably there will be developed a tar or pitch still in which it will be possible to produce coke of such a fineness and of such a low content of volatile matter that the operations of calcining and pulverization will be unnecessary.

Developments along the line of the newer ring-type of gas furnaces have made possible the reduction of the cost of the baking process. The hydrocarbon gases generated from the binder in baking are used as fuel for heating sections of the furnace, thus making a considerable saving in producer gas. There have been some minor developments along the lines of continuous electric furnaces (which is the superior baking method), with a view to recovering some of the enormous heat losses of radiation and cooling.

And last, but not of least importance, is the growing tendency for technical men in the industry to exchange information regarding the fundamental principles underlying the technology of carbon-electrode manufacture. Eventually this will result in greatly benefiting the industry as a whole and making it less and less of the "black art" which has characterized it in the past. Carbon plants are no longer regarded as fortifications; even visitors, within reason, are sometimes welcome, even if they come from competitors.

SÖDERBERG ELECTRODES

There has been developed within recent years a self-baking electrode formed continuously from a soft carbon mixture which is baked in the same furnace in which it is used. It thus provides a continuous electrode. The first electrode of this kind was built by Söderberg in 1909. Its commercial development took place between the years 1915 and 1919, when a 16-in. electrode was operated on a ferro-manganese

furnace without disturbance to the furnace and with no fracturing of the electrode. This electrode has since been running continuously and more than 1,000 ft. of linear length is stated to have been consumed in the same furnace without a single break in the electrode.

The Söderberg electrode is a continuous, jointless electrode which is built, baked and renewed right in the furnace itself in which it is used. The electrode consists of a ribbed cylinder of thin sheet iron, into which the electrode paste is filled. The electrode is added to from time to time by lengthening the cylinder and filling up with fresh paste. The paste for the electrode is the same and made in the same manner as previously described under electrode mixing practice. The lower end of the electrode is baked by waste heat from the furnace. In use, the electrode consists of a baked part and an unbaked part. The baking of the electrode takes place as it is allowed to slip through the holder. The holder is of the water-cooled clasp type. The slipping is effected by loosening the grip of the holder until the electrode slides by its own weight. Figure 85 shows the electrode holders employed on a 3-phase carbide furnace. This manipulation of the electrode may also be effected from a place situated at some distance from the furnace. Slipping of the electrode is carried on under full load. The current is maintained during slipping by means of a sliding contact between the holder and the electrode casing.

The organization which holds the patent rights on this electrode contends that, as the baking is done under the pressure from the paste above and proceeds vertically upwards, no pressing is required, and that the finished electrode will have as good an apparent density, conductivity, and crushing strength as that of ordinary electrodes. The use of Söderberg electrodes has been contemplated in alumina reduction. At the present time, one American manufacture is operating an experimental plant employing continuous electrodes. The first American installation was at a Southern alloy plant. A Mid-western carbide manufacturer is installing continuous electrodes.

Their use puts the electrode consumer in the electrode business to the extent either of manufacturing the electrode paste or of buying it. Until its use becomes more extensive,

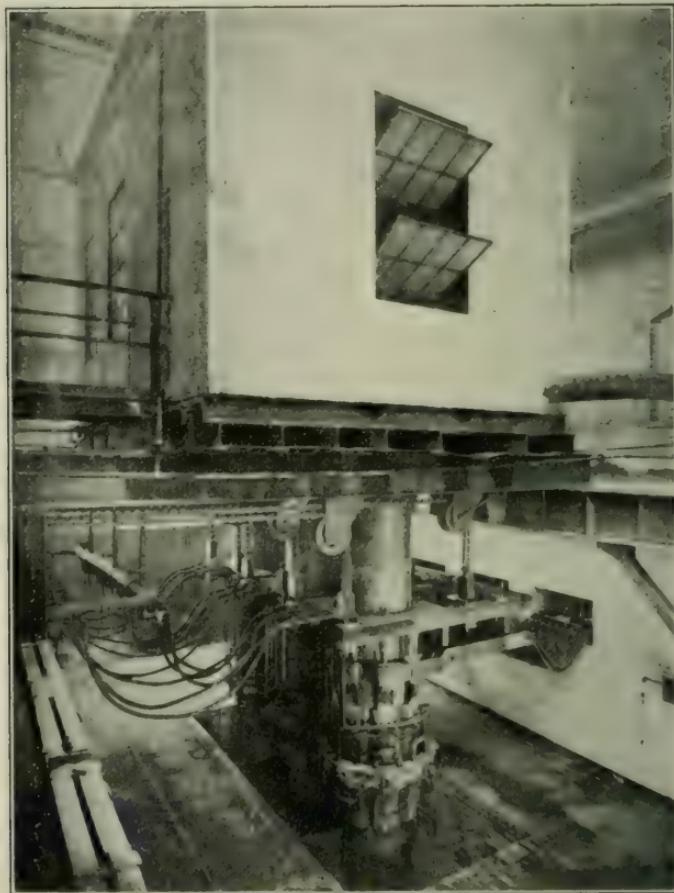


FIG. 85. — ELECTRODE HOLDERS EMPLOYED ON A THREE PHASE CARBIDE FURNACE
(Courtesy M. Sem)

it is questionable whether the Söderberg method produces electrodes of a quality equal to those produced by processes which preshape and bake the electrodes, as in ordinary practice previously described. Its advantage over present

day joined electrodes is that it allows the furnace operator to make his own electrodes in place. This is a questionable advantage, as it is quite likely that the electrode maker is a better manufacturer of his product, with a more highly developed technique, than a furnace operator would be.

The use of Söderberg electrodes has spread much more rapidly in Continental Europe than in the United States. Practically all the advantages of the Söderberg electrode are obtained in American practice with properly joined electrodes.

It is stated that the cost of the Söderberg electrode when mounted in the furnace is 75 to 80% of the price of ordinary electrodes.

The Söderberg electrode has possibilities of considerable expansion in its application. In isolated districts or in localities where shipping difficulties exist or sources of supplies from electrode makers are not readily available, it completely solves the problem of electrodes for the furnace operator. The making of the mix and the building up of the electrode are simple operations, readily handled by unskilled labor.

CHAPTER XXII

CARBON BRUSHES

THE manufacture of carbon brushes for use on electrical machinery is closely connected with the carbon electrode industry. Other than in differences in raw materials and the large amount of machinery work necessary before the finished product reaches the market, all the operations are the same or closely analogous.

In practically all forms of electric motors and generators, currents flow through conductors carried on the revolving part of the machine and in a majority of these machines the current must be conducted from an outside source to these revolving conductors, or vice versa. This is accomplished by means of a number of small pieces called brushes which bear against the revolving surface. Copper leaf and gauze were first used for this purpose, but as the size of the machines increased, they were found to be unsuitable, as they burned and wore the moving parts in contact with them. Carbon is the only material which combines the electrical and mechanical properties required for this purpose for nearly all machines. It may be and is at times combined with other materials such as metallic powders. Although the brush is small and simple in relation to the motor or generator on which it is used, the successful operation of the machine depends to a great extent upon the qualities of the brush. Poor or improper brushes can rapidly ruin parts of electrical machinery, as well as cause electrical troubles.

Carbon brushes came into use about 1890. At that time the limitations of metal brushes as then made for use with the larger sizes of machines, became decidedly apparent. The chief objection to metal brushes is that it is difficult to

keep the surfaces of commutators smooth when they are employed. The soft copper bars of the commutator and the metal brushes do not wear well. When soft metals are rubbed together or meet in a bearing surface, they always have a tendency to become rough. This extends so far at times as to cause pitting of the metal surface. The tendency of electrical machinery, particularly direct current generators, to spark at the brushes is greatly lessened by using brushes of a comparatively high resistance material (i.e. compared to copper) like carbon or graphite, instead of low resistance metal. Brush development has followed the rapid expansion of the electric industry and the extensive electrification of our age. Research and experimentation in the composition and manufacture of brushes have contributed largely to the development of electrical machinery.

The raw materials for brushes, as the result of manufacture of a wide range of products, with widely varying characteristics, are greater in number than those used for electrodes. The principle raw material is the same, however, being petroleum coke, the purest industrial form of carbon, available in large quantities. Other raw materials are lampblack, at times carbon black (very infrequently some of the other blacks may be used in small quantities) and in some instances retort or gas carbon, previously described under electrodes. Being a hard, dense material, retort carbon is sometimes employed to give a cutting grain to the brush and cause it to have slight abrasive action. Metallic powders, such as copper, zinc, lead and tin, either singly or together, are employed in the so-called metal carbon or metal graphite brushes. Graphite, — the natural variety to a greater extent, being either natural flake, Ceylon plumbago or Sonora (Mexico) amorphous, but also Acheson or the artificial variety to a considerable extent, — is an important brush raw material.

The raw materials are first calcined to drive off volatile matter and impurities. The methods and equipment are the same as for electrodes but the equipment is often of much

smaller size. In some small works the calciners may be coal fired. Lampblack and the graphites are ordinarily not calcined. When electric calciners are employed, products of varying resistivity may be produced by controlling calcining temperatures and length of time of the operation. The changes in resistivity are due to the degree of graphitization caused to take place.

The calcined materials are then pulverized to a flour and screened. The grinding is done in a wide variety of mills, the most generally used type is the roller mill with air separation and pulverizers of different makes. The procedure is similar to that of a wheat flour mill. The screened product is a fine carbon flour, the greater portion of which is 200 mesh or finer.

The dusts are weighed, the lampblack, graphite, metals, etc., according to the formula to be employed for the specific brush being made, are added and incorporated with the proper binders in steam-jacketed mixers, generally of the Werner and Pfleiderer type, as in electrode practice. The binders are coal tar pitches and coal tars. In some cases benzol, or a similar solvent is employed; in others summer oils or other types of tars are added. The practices of different brush manufacturers vary over wide limits. As in electrodes, one of the most important factors is the personal one; the human element and skill acquired by experience and actual contact with the working materials are invaluable when combined with good judgment.

Brushes are made either by molding or extrusion. If made by molding, they may acquire their final shape in the "green"; if made by extrusion, they are formed into rods which are later cut up.

If brushes are to be molded, the material from the mixer may be fed directly to the molding press and used as such, but generally, in order to acquire greater uniformity, the mix is allowed to cool and harden. The material is then reground, pulverized and remixed (sometimes more dust is incorporated, for a remixed material will take up more than was

possible to incorporate with the binder in the original mix). Brushes may be molded in multiple or singly. Figure 86 shows

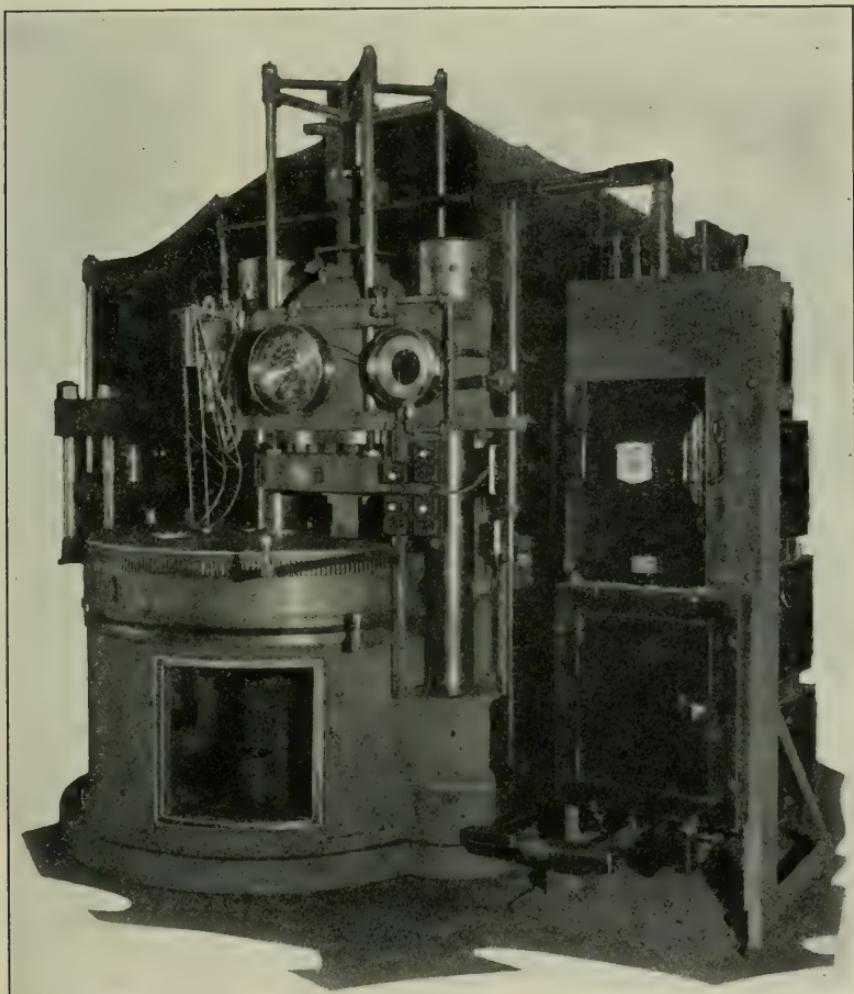


FIG. 86.—SEMI-AUTOMATIC BRUSH MOLDING MACHINE
(Courtesy Hydraulic Press Mfg. Co.)

one of the most modern semi-automatic brush molding hydraulic machines. These are in many cases self-feeding, automatic pressing and ejector discharging of the finished

product. In some other cases the hot material from the mixer is placed in steel molds, and molded in a hydraulic press under pressures of 10 to 20 tons per square inch into slabs of varying thickness but of more or less uniform surface (3" x 5").

When brush stock is extruded, the operations are identical with electrode making. Figure 87 shows a brush rod squirt-

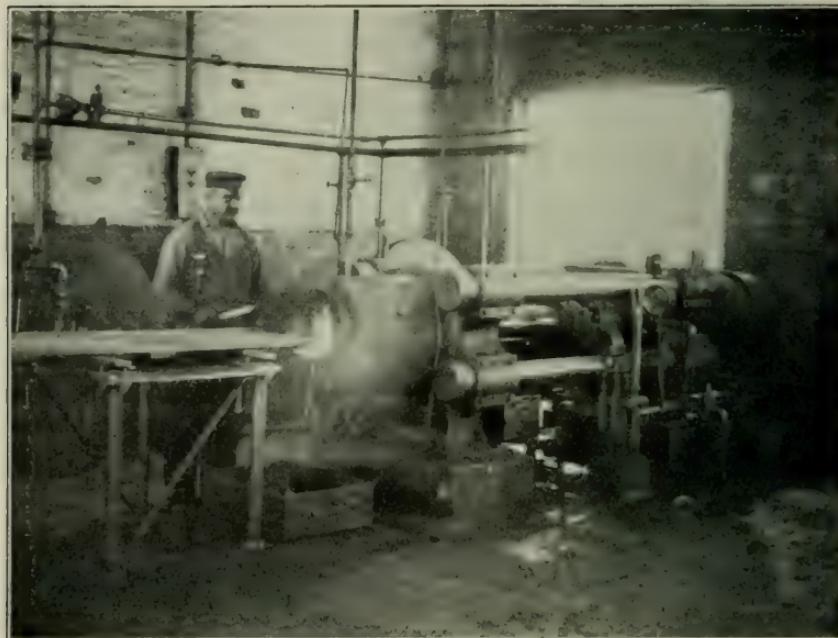


FIG. 87.—SQUIRTING BRUSH BARS OR BLOCKS
(Courtesy Stackpole Carbon Co.)

ing press. The dies are rectangular or round, depending upon the shape of the brush to be made. As the material comes out of the press it is cut by hand in pieces of proper length to be most expeditiously handled in further operations.

The green shaped pieces, either in the form of brush shapes, slabs or rods, are inspected and sent on to be baked. Brush baking furnaces are usually very much smaller in size than those employed for electrodes. The green stock is packed in

saggers, usually of refractory materials, with powdered calcined coke as a packing material. Temperatures are first raised slowly, then more rapidly after the preliminary coking of the binder. Final baking temperatures are from 1050° to as high as 1300° C. The length of time of baking will depend upon the furnace, its type, the charge, the method of heating, etc. In the highest type of brush, the electro-



FIG. 88.—CUTTING UP BAKED BLOCKS INTO BRUSHES AND GRINDING THE FACES
(Courtesy Stackpole Carbon Co.)

graphitic, baked blocks are graphitized in an electric graphitizing furnace. Baking furnaces for production of the ordinary carbon brush are of many types, either oil, gas, or coal fired, and in some few cases electrically heated.

After baking, the slabs or rods are cleaned of packing dust and cut into the required sizes by carborundum or other abrasive saws as shown in Fig. 88. They are smoothed and

then ground to exact size between high speed parallel wheels of abrasive composition. Sizes are controlled to within several thousandths of an inch to insure their proper fitting into the holders on the electrical machines for which they were made.

After grinding to size, the brushes are bored and countersunk for the pigtail (conductor) attachment. Certain types of brushes have their upper ends and pigtail socket copper electroplated, others tinned by hot dipping. This is done to insure perfect contact between the brush and the pigtail which is attached by either riveting or soldering. The brushes are then inspected, tested, stamped and sent to the consumer.

In general, the makers of electrical machinery do not make their own brushes, but purchase them from the carbon manufacturers. Another class of producers are the brush finishers who purchase carbon in the form of plates or rods and work it into shapes and sizes for brushes. There are a number of such companies, mostly small. Acheson Graphite Company finishes graphite brushes, graphitizing the formed products for other carbon makers.

Each grade of brush is described by its composition and by certain physical characteristics. These are determined by careful laboratory tests. If used properly they will materially aid in the selection of a grade of brush best adapted to a given service. The specific resistance is expressed in ohms per inch cube. The carrying capacity is the load current density the brush can carry without serious heating. Brushes are adapted only to ranges of commutator peripheral speeds and the same brush will not function properly at all speeds. The hardness of brushes, as determined by the scleroscope gives the following classification:

<i>Scleroscope Reading</i>	<i>Degree</i>
0 — 15	Very soft
16 — 30	Soft
31 — 45	Medium
46 — 60	Hard
61 or over	Very hard

Hardness of a brush is often considered an index of its abrasive qualities, but these two properties are entirely distinct. A very hard brush may possess very little polishing action on a commutator while a much softer grade may be highly abrasive. Hardness is a function of manufacturing processes; abrasiveness depends upon the constituent materials of the brush.

By abrasiveness is meant the mechanical grinding and polishing action a brush exerts on the commutator. Other factors such as the polish on the commutator and brush faces, peripheral speed, brush pressure, etc., influence the abrasive effect of the brush so that it is practically impossible to employ an arbitrary scale to classify varying degrees of abrasiveness. Often the operating conditions cause the brush to appear more abrasive than it really is. If subjected to very heavy and quickly applied overloads, a non-abrasive brush may become slightly abrasive. The action is then due to the electrolytic action between the brush face and the commutator, caused by the heavy short circuit current when the overload is taken on or dropped off. The brush picks up copper, which causes it to wear the commutator.

One of the largest manufacturers of brushes, the National Carbon Company, classifies its products as follows: — abrasive, when the brush is capable of keeping down mica on slow speed commutators operating under severe electrical or mechanical conditions; medium abrasive, when suitable for medium speed commutators (up to 3500 ft. per minute) under normal operating conditions; slightly abrasive, for medium to high speed peripheral speeds; polishing, where commutating conditions are good at medium and high speeds, and on slotted commutators in hard service where there is a tendency to form smut on the commutator or collecting ring; slight polishing, employed on slotted commutators; non-abrasive, such as the electrographitic, completely graphitized, brushes where the wearing and polishing effect is at a minimum. The brush will cause the commutator to assume a fine glossy chocolate color, and, if commutation be good, to remain in this condition indefinitely.

The contact drop is the voltage lost between the face of the brush and the commutator. Atmospheric conditions have a marked effect on contact drop. The values given in the table of brush characteristics are only comparative. They were obtained under almost ideal conditions in the laboratory, and could not be checked on commercial machines in ordinary operating practice.

The coefficient of friction of a brush is the ratio of frictional force to normal pressure. The cotangent of the angle (to the commutator) at which the brush just floats in its holder can be shown by theoretical considerations, to be the coefficient of friction. In general, the coefficient of friction decreases with increase of pressure on the brush. In some cases the brush and commutator contact is so intimate that a partial vacuum is formed underneath the brush, with resulting decrease of friction. Some types of brushes show this effect in a more pronounced manner than others. The coefficients of friction given in the table were determined under almost ideal laboratory conditions.

A summary of the average characteristics of the standard grades of brushes of the largest American manufacturer (The National Carbon Co.) is given in the table below:¹

The carbon-graphite brush is usually termed a "carbon" brush. It consists principally of amorphous carbon (calcined petroleum coke) with sufficient added graphite to increase its conductivity and lubricating properties. Natural graphite is generally used. Since this material contains appreciable ash, this type of brush will have considerable abrasive action.

Manufacturers and users quite commonly impregnate carbon brushes with lubricants to reduce friction, temper the abrasive action and improve commutation, due to the contact resistance caused by the film of lubricant at the brush face. At high temperatures such brushes lose the lubricant. They show a tendency to collect dust which may be of an abrasive nature, as well as to collect copper on the brush face.

¹ National Carbon Products (1924), National Carbon Co., Cleveland, Ohio.

TABLE XXX
AVERAGE CHARACTERISTICS OF STANDARD GRADES OF BRUSHES

Grade	Specific Resistance (Oms per In. Cube)	Carrying Capacity (Amps. per Sq. In.)	Peripheral Speed (Ft. per Min.)	Hardness Sclerometer	Strength (Lbs. per Sq. In.)	Contact Drop, Laboratory Average	Coefficient of Friction	Abrasiveness
Carbon-Graphite (artificially lubricated)	0.0015	40	3000	40	3600	0.81	Below 0.22	Abrasive
	0.0015	35	3500	45	3650	0.61	Below 0.3	Medium abrasive
	0.0014	45	3500	40	4400	1.11	Below 0.22	Medium abrasive
Graphite-Carbon	0.0011	35	4000	50	3200	0.56	Above 0.3	Medium abrasive
	0.00077	35	3000	42	3700	Below 0.5	Above 0.3	Slight abrasive
	0.0010	45	3500	53	5500	0.54	Above 0.3	Slight abrasive
Electrographitic (partially graphitized)	0.0008	40	4000	42	6000	Below 0.7	Below 0.3	Slight abrasive
	0.0011	45	4000	40	3500	0.39	Above 0.3	Slight abrasive
	0.0018	30	4000	81	5500	0.97	Below 0.22	Slight polishing
Special purpose graphite	0.0016	40	3500	74	5800	0.80	Below 0.3	Polishing
	0.0013	45	4000	60	5500	0.81	Below 0.3	Slight polishing
	0.0022	30	4000	77	5000	0.71	Above 0.3	Medium abrasive
Electrographitic (graphitized completely)	0.0014	40	3500	84	8000	0.73	Below 0.3	Medium abrasive
	0.00043	55	3800	27	4600	1.01	Below 0.3	Polishing
	0.00055	60	6000	16	2100	0.62	Above 0.3	Slight abrasive
Metal graphite	0.00049	65	6000	15	1700	0.45	Above 0.3	Slight polishing
	0.0012	60	12000	16	1100	0.29	Above 0.3	Slight polishing
	0.0012	45	4500	72	5900	0.86	Below 0.22	Polishing
	0.0018	55	5500	66	3600	0.86	Below 0.22	Non-abrasive
	0.0007	60	5500	42	5100	0.90	Below 0.22	Slight polishing
	0.0018	60	6000	55	2900	0.92	Below 0.22	Non-abrasive
	0.00006	125	4500	20	5000	0.31	Below 0.3	
	0.000025	150	3500	12	12000	0.03	Below 0.3	
	0.000021	150	4000	9	8000	0.05	Below 0.3	
	0.000047	115	6000	19	4900	0.22	Below 0.22	

"Carbon" brushes are within the medium range of hardness, of low carrying capacity, and not adapted to high peripheral speeds. They are employed on flush mica commutators, being not adapted to slotted types due to their abrasiveness and lubricants. They must be classed, however, as a good all-round brush, of moderate price, as they will perform satisfactorily within the limits of their characteristics over a wide range of conditions.

The graphite-carbon brushes are those in which a large or the greater percentage of material of composition is graphite, the remainder being coke or other forms of amorphous carbon. These contain sufficient graphite for lubrication. Artificial as well as natural graphites are used, depending upon the desired characteristics of the finished product. The abrasive qualities will vary with the quality of the original graphite used. They are usually hard with carrying capacities the same as or higher than the "carbon" brushes. The contact drop is low or very low. They find extensive application on industrial motors, moderate speed generators, mining and mill service and railway motors. In their small shapes, some grades are well adapted to fan motors and small domestic motors where long life is essential. They are medium priced and cover a broad field of application.

There are numerous grades of brushes composed entirely of graphite except for the bonding material. These have high carrying capacity, medium contact drop and low coefficient of friction, adapting them to high commutator speeds. A few grades possessing low specific gravity to reduce brush inertia at high rotative speeds exist. Others of rather limited field of application, manufactured by special methods, give materials of very high resistance and some better commutation.

Most brushes of the graphite class are non-abrasive or with a polishing action, or at most but slightly abrasive. They are generally used on undercut mica commutators, but a few of the slightly abrasive grades can be used, when condi-

tions are not severe, on flush commutating surfaces. They possess low mechanical strength and are incapable of meeting severe mechanical conditions. This type has much in its favor where quietness of operation is desirable. They are employed to a considerable extent on turbogenerators and other high speed machines, automotive lighting generators, electric vehicle and battery locomotive motors, battery charging and other low voltage generators and similar machines.

The electrographitic brush represents the highest stage of manufacture. This type is made of carefully selected forms of amorphous carbon to give the desired characteristics of the finished product. In the final baking, temperatures are regulated as well as time of exposure, so as to graphitize all or part of the amorphous carbon. When entirely graphitized, the brush is as near being absolutely non-abrasive as it is possible to be made. It is also made with varying degrees of abrasiveness to meet special conditions. This class of brushes is hard and in some grades very hard. They are mechanically strong and tough, with high conductivity due to the dense structure. Their commutating properties are above average, with very high contact drop obtainable without the use of impregnating materials. Combined with the low coefficient of friction and high carrying capacity, this property gives an ideal set of brush characteristics, making certain grades adaptable to a very wide field of applications.

Electrographitic brushes have been employed on practically all known types of machines except plating generators. The only wear to the commutator which will occur due to their use is the relatively small electrolytic action of the current. The non-abrasive grades are adapted to undercut commutators. The hardness of the brush gives a cleaning and polishing action to the commutator. Due to its ruggedness, the electrographitic brush is applicable to collector rings under severe mechanical conditions. Current densities up to 80 amperes per square inch are used on the A.C. rings of rotary converters. Where excess heating has caused com-

mutator trouble, the problem has been solved by the employment of entirely graphitized electrographitic brushes.

At times, and in certain classes of service, a brush contact drop much lower than that of any carbon brush yet higher than that of metal is required. Brushes are made for this purpose of a graphite and metal powder mix, the metals being copper, tin, zinc or lead, or copper alloyed to some extent with these metals. Pure copper powder, owing to its tendency to cut rings, does not make the best brush for use on slip rings. The alloys or mixtures with other metal powders make a brush less liable to score the rings. These brushes are molded at high pressures. In some cases the binder is omitted, the temperature in baking being raised high enough to cause partial fusion of the metals which then serve as the binder. These brushes have very low contact drops, but values higher than pure metal brushes. They make it possible to secure good commutation on low voltage machines, while the graphite is a good lubricant. They can be employed on commutators and slip rings at high peripheral speeds without difficulty.

Morganite (Morgan Crucible Co., London) is a composition brush. The brush is constructed in layers in such a way that the resistance across the brush is from seven to eight times that in the opposite direction. In this way a path of high conductivity is provided for the current in the external circuit, while the cross resistance of the brush tends to reduce the current in the short circuited coil. The brushes consist of Ceylon or flake graphite ground to 100 mesh and molded under a pressure of 20 tons per square inch. Metal-graphite Morganite brushes are made in the same way.

Present tendencies seem, according to Kalb,² to be away from the use of metal graphite brushes on slip rings and toward the use of graphite and electrographitic brushes at current densities suited to these grades. There are many things to be said in favor of this. A serious objection, however, is met in induction motors of the slip ring type where

² Power, (February 18, 1919), p. 241.

it is desired to keep the slip at as low a figure as possible. Here the higher contact drop of graphite and electrographitic brushes will cause a greater percentage of slip than found with metal graphite brushes.

All carbon brush manufacturers now standardize the size of their carbons to a limited number of dimensions to eliminate the cost of preparing and keeping in stock the thousands of sizes formerly employed, when everyone who designed an electrical machine seemingly thought it incumbent upon him to design a new or a special sized brush. The lengths of round and rectangular brushes up to and including $1\frac{1}{4}$ inch increase by $\frac{1}{8}$ inch steps, then by $\frac{1}{4}$ inch steps to 3 inch length, then by $\frac{1}{2}$ inch steps to greater lengths; preference being given to $\frac{1}{4}$ inch steps below 1 inch and $\frac{1}{2}$ inch steps above. The widths increase by $\frac{1}{16}$ inch steps up to $\frac{1}{4}$ inch, then by $\frac{1}{8}$ inch steps to $2\frac{1}{2}$ inch width or diameter, and by $\frac{1}{4}$ inch steps above that, preference being given to $\frac{1}{4}$ inch steps wherever possible. Round brushes vary by $\frac{1}{8}$ inch steps of diameter. Thicknesses increase by $\frac{1}{16}$ inch steps up to $\frac{3}{4}$ inch, and then by $\frac{1}{8}$ inch additions. Bevels vary by five degree additions. The length of a beveled brush will be that of the square ended brush from which it was made.

The brush industry, while a very much smaller tonnage industry than electrodes, manufactures products commanding many times the price per pound value of electrodes because of the greater amount of machine work necessary and the smaller tonnage output per worker. Brushes are made to the amount of six to ten million dollars annually in the United States.

CHAPTER XXIII

ARC LIGHT CARBONS

ARC light or electric lighting carbons are cylindrical rods used for the production of the arc light. Two carbons, connected to a source of current are brought together, end to end, completing a circuit and starting a current flow. When they are separated slightly an arc is formed, a portion of the carbon is vaporized and the current continues across the bridge of carbon vapor.

Carbon arcs are of two types. In the ordinary arc, the light is produced by the high temperature to which the end of one or both of the carbons is raised. In the ordinary form the arc of carbon vapor gives very little light, but by adding certain salts to one or both of the carbon rods, the hot vapor becomes very luminous, producing the flaming arc. The salts added are vaporized by the arc temperature. Much more light is obtained from the flaming arc than from the ordinary type for a given amount of electrical energy consumed. There is now another type of arc, more widely used for street lighting than the carbon arc. This is one which employs magnetite in a luminous arc and no carbon is used or needed.

The founder of the arc light carbon industry, from whose work most of the development of the entire carbon products industry arose, was the Frenchman Carré.¹ His work and that of Fontaine, Foucault, Curmer and others have been dealt with under electrode historical development. Pritchard² in 1890, Jehl³ in 1899, and Ornstein⁴ in 1900 gave

¹ Comptes Rendus, Feb. 19, 1877.

² Manu. of Elect. Light Carbons, London, 1890.

³ Manu. of Carbons for Elect. Lighting, etc., London, 1899.

⁴ Fabrication d'Electrodes, Paris, 1900.

accounts of the early English and French developments while Härden⁵ in 1901 and Zellner⁶ in 1903 described German practice. Jasche⁷ covered the effect of metal salts on arc light carbons, Brandt,⁸ Blumenthal,⁹ Siemens Brothers¹⁰ Czudnochowski,¹¹ Rasch¹² and Monasch¹³ extensively described the manufacture and preparation of arc light carbons between 1901 and 1910 when they were of great importance for street lighting.

Brandt,¹⁴ Bohm,¹⁵ and Bay¹⁶ described in great detail the Continental practice over the period of 1910 and 1916, when there were numerous advances in manufacturing technique and commercial application. Hardman¹⁷ described American search light carbon manufacture and testing.

In the earlier period of arc lighting, the manufacture of carbons was developed further in Europe than in America. Some types of carbons could not be obtained in the United States of a quality as high as that of the foreign article. The American industry advanced by leaps and bounds during the war. At the present time foreign-made carbons have no superiority over American-made articles.

⁵ *Electrotechn. Ztschr.*, vol. 22, pp. 300 and 584 (1901).

⁶ *Die Künstlichen Kohlen*, Berlin, 1903.

⁷ Dissertation — Breslau, 1904, — "Spectrophotometrische Untersuchungen über den Einfluss der Beimischung von Metallsalzen zu Bogenlichtkohlen auf die Verteilung der sichtbaren Energie in den einzelnen Teilen des Spektrums ihrer Flammenbogen."

⁸ *Chem. Ztg.* (1901), p. 980.

⁹ *Die Bedeutung der electrotechnischen Spezialfabrikation für Starkstrom Erzeugnisse*, Berlin, 1905.

¹⁰ *Herstellung und Gutprüfung von Bogenlichtkohlen*, Berlin, 1906.

¹¹ *Das Electrische Bogenlicht*, Leipzig, 1906.

¹² *Das Electrische Bogenlicht*, Braunschweig, 1910.

¹³ *Illum. Eng. (London)*, vol. 3, pp. 253, 394, 427.

¹⁴ *Electrotech. Ztschr.*, vol. 32, p. 1183 (1911); *Helios*, vol. 22, pp. 25 and 38 (1916).

¹⁵ *Die Verwendung der seltenen Erde*, Leipzig (1913); *Chem. Ztg.*, vol. 40, pp. 637-9, 655-7, 667-9, 690-3 (1916).

¹⁶ *L'Electricien*, vol. 37, pp. 358-60, 379-82, 396-98, and 404-5.

¹⁷ *Gen. Elec. Review*, vol. 22, pp. 685-7 (1919).

Both the ordinary and the flaming carbon arcs are of two kinds, — the open arc which burns in the open air, and the enclosed arc in which the circulation of air is prevented by a tight-fitting glass glove. The effect of enclosing the arc is to reduce the efficiency but greatly to increase the life of the carbons.

Each of the different types and kinds of arc requires a carbon of certain composition. Further, there is required a large variety of carbons, the choice of which depends upon the purpose for which the light is to be used. For many applications, the central portion or core of the carbon is of material different from that of the shell. It frequently contains softer material, or salts, in order to hold the arc steady at the center of the rod. It may also contain the flaming material if this be used.

Electric lighting carbons were first used in the open arc which came into use before 1880. They were made of retort carbon or petroleum coke. The original arc carbons on the Continent were cut from chunks of hard retort coke. They were exceedingly liable to split, crack and break, and in general were far from being satisfactory. Several years later lampblack was found to give better results. About 1895, the closed arc was introduced. Lampblack carbons were necessary for this type, owing to the greater purity desired. The use of the open arc, and with it the demand for petroleum coke carbons, declined rapidly. About 1905, the introduction of the magnetite arc, requiring no carbon, and the high powered tungsten incandescent lamp a little later, caused a greatly decreased use of the ordinary arc as the more efficient units replaced arc lamps. In the meantime the flaming arc was developed. It had a short history as a street and general illuminant. Industrial uses were found for the open flame arc, employing a carbon with a lampblack shell and a core of flaming salts. The motion picture industry also came into existence, using both the ordinary open arc and the open flame arc. At the present time the carbon arc for street and general interior lighting is practically a thing

of the past, due to its almost complete replacement by the magnetite arc, and more especially by the tungsten incandescent. The development of the latter, in the form of Klieg lights, has almost entirely eliminated arc lights from the motion picture industry.

Petroleum coke, in America at least, was the material from which carbons were first made on a commercial scale. They were used in the open arc lamps in which the life of a pair of carbons was only a few hours, so that the number of these carbons used was large. The quantity rapidly declined with the passage of the open arc.

Lampblack was first used for the open arc, as the light obtained was superior to that of petroleum coke carbons. Abroad lampblack carbons were used for this lamp to a much greater extent than in America, as the open arc was retained there longer because of cheaper labor for maintenance.

When the enclosed arc began to replace the open, it was found that petroleum coke, because of its ash content, was not sufficiently pure for this lamp. Lampblack was found to be necessary.

The raw materials for making arc light electrodes of various types are lampblack, retort carbon, petroleum coke, pitch coke in some cases, tar coke and tar soot on the Continent, as body materials, with pitches, tars and related materials as binders. The processes of manufacture are analogous to those of electrodes. Böhm¹⁸ states that a good mix is 100 parts crude soot (lampblack), 100 parts treated soot, 1 part of boric acid and 160 parts of tar. His "treated soot" was made by mixing 100 parts of "soot" with 130 parts of tar, forming into blocks in a hydraulic press, baking these at 1,000°–1,400° F., and then grinding to pass a 300 mesh sieve. He states that a good mixture for coke carbons is 100 parts of coke powder, 100 parts powdered coke electrodes (both 100 mesh), 60 parts treated soot, 40 parts raw soot, 3 parts boric acid and about 155 parts tar.

¹⁸ Chem. Ztg., vol. 40, pp. 637–9, 655–7, 667–9, 690–3 (1916).

The materials used for the production of white light are titanium, thorium and cerium oxides, monazite sand, ilmenite, lime, ferrotitanium, various metallic oxides and related materials. The United States patent literature gives a large and varied list of materials. Silicate of soda has generally been used as the binder but sometimes dextrines, caseins, water soluble gums and at times milk of lime as well as clays have been employed.

The materials, after calcining, are mixed together and, if homogeneous carbons are to be made, the salts or oxides are added and incorporated. This type of carbon, employed in the enclosed flaming arc, is now little used. The rods or shells are extruded. The formed sections are packed in packing dust and baked in saggers in coal or gas fired furnaces. Böhm states that a good sagger can be made with 30 parts kaolin, 20 parts high grade fire clay, and 50 parts grog. The saggers are formed, air dried, glazed and kiln fired to at least 1,300° F. After baking, a careful inspection of the product is made. The carbons are then cut into the desired length, sorted, pointed and smoothed by special machinery, some of which is highly automatic. In some cases the cores of the carbons are filled before baking, in other cases after baking. Careful and trained supervision is necessary throughout all stages of the processes. A great amount of technical research has been carried out to determine the most desirable composition and methods of treatment.

For many projectors, lampblack carbons are necessary to obtain a light of the required steadiness and brilliancy. For many purposes these carbons are made with a central core containing chemicals for steadyng the arc (but not for increasing the light as in the flaming carbons) and are known as cored carbons. The use of lampblack carbons for enclosed arcs is rapidly decreasing. They are still employed in considerable numbers in motion picture projectors, although for this purpose they will probably be superseded by the flaming arc.

Flaming arc carbons are made with shells of lampblack and cores of chemical salts. They are a most desirable source of light for both motion picture and general photography, and effects can be obtained by their use which would not be obtainable by any other means. Photoengraving is largely done by the flaming arc. The high powered searchlight is another of its important fields. Other uses are in paint and dye testing and certain forms of chemical manufacture. Blue-printing machines use arc carbons for light sources. They are employed to some small extent on headlights on street railways and similar applications.

CHAPTER XXIV

CARBON SPECIALTIES

CARBON specialties are articles of carbon, molded in special shapes to predetermined characteristics or else machined out of stock shapes to supply a specified demand.

The non-fusing characteristics of carbon are made use of in carbon and graphite contacts used on electric elevator controllers, automatic motor starting equipment, high amperage circuit breakers and the like, where a non-burning material is essential to long life of the contact. The suitability of carbon for this purpose is due to its electrical conductivity and its ability to withstand the action of the electric arc. Contacts are made of carbon or graphite, depending upon the carrying capacity necessary in the particular case. The products are made by molding or grinding and machining. They are made in a variety of shapes and sizes to conform to the demands of different electrical designs. In general their properties are quite similar to those of brushes.

Rheostat disks and plates are made of carbon for the types of electrical apparatus requiring very accurate current control, inasmuch as carbon plate rheostats are the only kind which are sufficiently fine in their graduations to be considered satisfactory for this service. Carbon disks and plates are being extensively used for train lighting control, battery testing sets, voltage and current control in the laboratory, motor starters and many other similar applications. The carbons are made by molding directly or by cutting and machining from larger size stock. Resistance can be varied by variation of the pressure on the pile. The plates are made in either plain or corrugated shapes. The

latter are more efficient in dissipating heat. They are widely used in testing sets.

The telephone transmitter consists essentially of two thin carbon disks, the space between being filled with granular carbon. Sound waves cause variations in the pressure between the granules which produce corresponding variations in the electric current flowing through them. The variations of the current produce corresponding sounds at the receiving end of the line. The disks must be hard and highly polished.

Telephone granular carbon is a crushed product, made from petroleum coke or selected coals, electrically calcined to determined resistivity, vacuum treated, ground and sifted to sixty to eighty meshes to the inch in its use for ordinary telephones, and sixty to one hundred twenty mesh for some special purposes. It must be hard material. The shape of the particles is of considerable importance. The characteristics of the finished product are carefully regulated by intensive control of all manufacturing operations. Telephones for the deaf and for certain commercial purposes require diaphragms and back plates of carbon, the space between being filled with a special hollow globular form of carbon granules.

Plungers of graphite are extensively used in dashpots where it is not desirable to use oil for various reasons or where inspections are very infrequent. They find their widest applications where a dry plunger is necessary to insure continuity of service, such as the dashpots of arc lamps or on train lighting equipment.

The extreme resistance of carbon to fusing is utilized in protecting telephone apparatus from abnormal rises of voltage by providing a means of discharge to ground through carbon "lightning arresters."

Carbon is especially suited for use as a packing in the shafts of steam turbines, to prevent steam and air leakage. Rings are made up (by molding in most cases, with subsequent machining) in segments to fit the shaft, against which they are held by coiled springs. They are made of a

high grade dense carbon and operate without wearing the shaft. They are resistant to the breaking-down action of hot air, superheated steam and oil. These are decidedly detrimental in their action on other types of packings. Graphite and lead packing rings are employed on high pressure hydraulic machinery, giving satisfactory results where other packings do not stand up over long periods. The powdered mix of graphite and lead is shaped by molding under high pressures.

Porous carbon pots for electric batteries are hollow cylinders of carbon, open at the bottom, and having a hole at the top, provided with an insulating bushing, through which a zinc rod is inserted. They are used in the wet form of battery, which was in general use before the introduction of the dry battery. They are not now of much importance, as the improvement and general adoption of the dry battery have caused it to supersede the older form entirely.

Carbon specialties assume a great number of forms, shapes and sizes. Some of the more common ones are shown in Fig. 89.

The principal materials used in the manufacture of carbon specialties are petroleum coke, lampblack, graphite, retort carbon, metal powders, with pitches and tars as binders. The graphite employed is both natural and artificial. Some carbon specialties are graphitized in electric furnaces; others are machined out of blocks or rods of artificial graphite. The selection of the raw materials is of great importance in obtaining products of uniform quality. The products may require machining or polishing or both, according to the use for which they are intended.

The development of the carbon specialties manufacture is to a great extent coincident and contemporary with the growth and expansion of the dry battery industry, the telephone and other electrical equipment. These call for the greater part of the production.

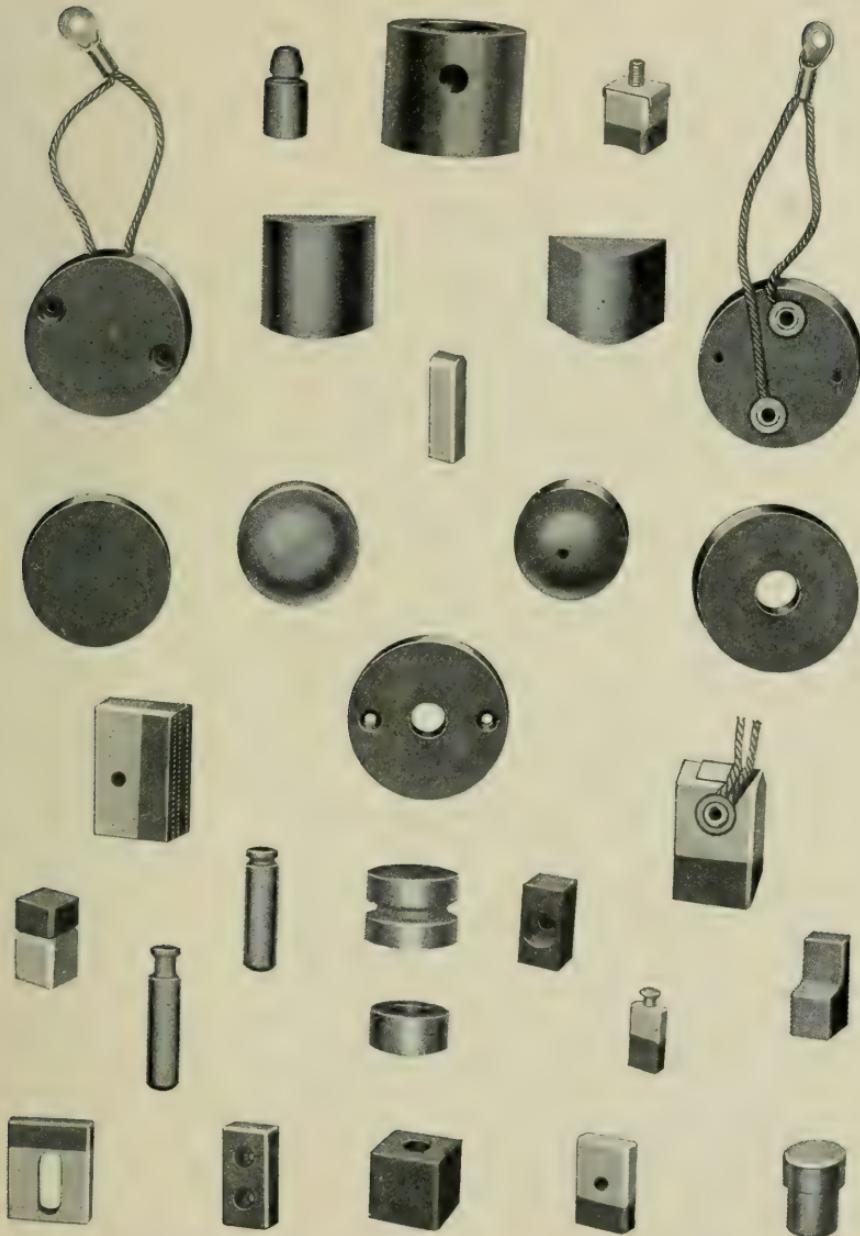


FIG. 89.—SOME FORMS OF CARBON SPECIALTIES
(Courtesy Ohio Carbon Co.)

CHAPTER XXV

BATTERY AND WELDING CARBONS

BATTERY carbons are in reality small sized electrodes. The raw materials and processes of manufacture are quite the same. They are made by molding and extrusion, the latter being the more preferable method since unusual corrugated shapes are not used to a great extent at the present day. In portable or small sized dry cells of the Leclanché type, they form the positive pole of the cell. These are the common dry batteries for bell ringing, annunciators, signaling, etc., and the radio battery made in tremendous quantities by connecting small units together and assembling them in cases. In the cell they are surrounded by a depolarizing mixture containing, among other things, artificial graphite powder or coke calcined to definite resistivity by partial or complete graphitization. Since they are not affected by oxidation as are furnace electrodes, the matter of obtaining high apparent density in manufacture is not so important. Resistivity must be definitely controlled and is of considerable importance. The size of grain may affect the quality of the battery.

Welding carbons are carbon electrodes used in welding metal. They serve as conductors of current and as one pole of the welding arc. They are made either of amorphous carbon rods or of artificial graphite. Their mechanical strength and conductivity are carefully regulated.

CHAPTER XXVI

PENCILS

THE manufacture of so-called lead pencils on a commercial scale originated in England in the reign of Queen Elizabeth. At that time (1564) the famous Borrowdale graphite deposit in Cumberland was discovered. Much of the graphite of this deposit was of such purity that it could be taken out in large blocks and cut up into pencil rods. It was not necessary to subject the material to any refining process. The graphite that was too impure, as a result of the admixture of other minerals, to be suitable for pencils was used for crucible making.

As everyone knows, there is no lead in a lead pencil, that is, no metallic lead. The lead of a pencil is made of graphite mixed with special kinds of clay.

The high grade pencil graphite from the Borrowdale mines was highly prized. It brought such high prices that a great deal of trouble arose regarding titles and ownership of the mines. Eventually the government was forced to assume control of the deposits. A period of six weeks was set as the maximum time during each year that the mine might be worked. Even under this limitation the average annual output amounted in value to £40,000.

All of the graphite produced was sent to the London auctions held on the first Monday in each month. It commonly brought as much as \$40 per lb. The government soon prohibited all exports of graphite except in the form of pencils, so that the new industry might be fostered.

After the richer portions of the Borrowdale deposits were exhausted, attempts were made to concentrate the poorer ore. The material so obtained never equalled the richer grades of crude graphite.

The last active work in the Borrowdale mines was carried out in 1833. Some prospecting was done in 1875 and the graphite obtained is reported to have sold at \$10 per lb.* The mineral occurred in pipes, strings and nests in association with a dike of altered diorite intruded into volcanic ash.

The occurrence of similar material was discovered at Mount Batougol in Siberia at just about the time when the Borrowdale deposits became exhausted. The Siberian mines for many years supplied the Faber pencil factory at Nürenberg with all the graphite required.

The first pencils consisted merely of rods of pure graphite cut from the massive mine material. Later these rods were inserted between pieces of grooved wood, forming pencils of the same type as those used at the present day, although they were probably larger and contained thicker leads.

This raw graphite had so many limitations as a marker and yet so many evident possibilities that various methods were tried to increase its serviceability. To obtain a harder lead, the graphite rods are reported to have been heated in molten sulphur before being placed between the wood strips. Pencils continued to be made in this manner up to 1795 when Conte devised the present method of manufacture. This consists of powdering the graphite, mixing it with a finely ground clay so that a thick paste is made, the leads then molded or shaped in some other manner, and afterward baked. This made a much more uniform product possible. Changes of the proportions of clay and graphite in the mixture allowed the production of varying degrees of hardness.

This method naturally effected a great saving in graphite over the old procedure which was obviously very wasteful. Attempts had been previously made to eliminate the waste from the Borrowdale graphite mines by pulverizing and subjecting the material to a chemical process to remove the gangue. The graphite sludge was then pressed into a compact mass which could be cut in the same way as was the natural mineral. This method was not successful, nor were

later attempts to incorporate glue, isinglass, tallow, wax and other bonding substances into the powdered graphite in order to form a compact sectile mass. Equally unsuccessful was the experiment of mixing graphite with melted sulphur or antimony.

At the present day, only the soft, earthy, or so-called amorphous graphites are used in pencil making. The flake graphites as well as Ceylon plumbago do not possess nearly the same marking power as the earthy kinds, of which the Siberian and Mexican are examples. Mexican graphite forms the bulk of the raw material used in American pencil factories. The Bavarian and Bohemian mineral is also well suited for this purpose. Faber at Stein near Nürenberg in Germany, and Hardmuth at Vienna in Austria, were for years the largest pencil manufacturing concerns in the world. In the early nineties the industry obtained a foothold in America. Within three years the exports of pencils from Germany to the United States dropped off almost one half.

It is estimated that about 8% of the total world's production of graphite is consumed in pencil manufacture.

Modern methods of pencil making employ a soft amorphous graphite which may be more readily ground to a powder of uniform particle size. Flake graphite, no matter how finely ground, still preserves its flake or lamellar form. Clay is the binding element, and the proportion of clay determines the hardness of the lead. Much attention is devoted by manufacturers to producing extremely high grade pencils especially adapted to different classes of sketching and drafting work. The correct mixing of the graphite and clay is given the closest supervision. One of the larger United States firms offers 17 grades of hardness in its best grade of pencil. The maintenance of strict uniformity throughout the different hardnesses requires the closest attention to the quality of raw materials, the grinding, mixing and proportioning.

The graphite is ground dry, then air floated and finally

water floated to remove grit particles. A high grade stone-ware clay free from iron and lime, highly plastic and refractory, is used as the binder. A suitable clay should contain from 50 to 60% silica and 40 to 50% alumina. The clay is ground dry, water floated and settled in tanks. Graphite and clay are then mixed mechanically and ground between burr stones in a closed tank. This grinding is wet and, according to the degree of fineness required, lasts from two weeks to three months. Some plants, instead of using burr stones, use pebble mills or tube mills. Flint pebbles act as the grinding medium. In the case of tube mills, the grinding is done in closed system. After grinding, the sludge passes to filter presses or vacuum filters. The latter is preferred since filter press cloths or screens tend to clog with the exceedingly fine product. Excess water is sometimes removed by hydraulic dewatering presses and the mass compressed. The product from the presses is kneaded to the required consistency. The plastic mass is then run through one hydraulic press after another to secure still further and further compression, and finally it is forced through dies of the diameter of the finished lead. These presses are of the squirting or extrusion press type similar to those used for small electrodes and arc light carbons. Extrusion pressures are of the order of 800 to 2,000 lbs. per sq. in. or slightly above. The dies are of hardened steel or in some cases of drilled diamonds and sapphires. Lead issues from the die in the form of a continuous string. The die head is mounted on a toggle joint so that the string is coiled as it comes out of the die and is caught in a shallow metal dish. The dish is removed when full. The lead is uncoiled by hand and pinched off into lengths each equal to three pencil lengths. The material is quite tough and pliable. It may be readily handled without breaking or deformation. Lengths of lead are laid between boards and allowed to air dry. In some factories the extruded lead as it comes from the die is curled out onto a carrying board instead of a tray. After they are air dried they are cut by hand into pencil

lengths and arranged in bundles in graphite boxes. They are then kiln baked for several hours at temperatures of 1,500 to 2,000° F. and cooled out of contact with air. They are now ready to be placed in the wood casings. An intermediate drying may take place before the final baking. This is often effected in iron boxes in a hot air chamber at 150° F.

The wood casings consist of blocks of cedar measuring 7 $\frac{1}{4}$ " by 2 $\frac{1}{4}$ " by 3 $\frac{3}{16}$ " in each case. These are grooved to receive the leads. Each block is provided with six grooves, and after insertion of the leads the blocks are dipped in glue and clamped together in bundles. After the glue is set, the blocks are cut up into the individual pencils which are trimmed, sandpapered, painted, varnished and stamped.

The softer grades of pencils have leads of greater diameter than the harder grades, as they are not mechanically as strong.

A common proportion in pencil making is three parts of clay and two of graphite. Sometimes antimony sulphide, lampblack, carbon black and even finely divided metallic lead are incorporated in the mixture. A number of manufacturers boil the leads in baths of wax or tallow in order to remove grittiness or to add further to their strength and smoothness. This operation is done before the leads are put in the wooden casings.

Copying leads are made by the use of methyl violet combined with graphite and other materials. Colored crayon lead pencils are made by the substitution of a finely ground color pigment for the graphite, together with properly selected and refined clay.

Artificial graphite is not considered well suited for pencil manufacture as it is apt to contain particles of carborundum. In the better grades of artificial graphite, however, this objection does not hold true.

The greater bulk of the pencil graphite consumed on the North American continent comes from mines in Central Sonora, Mexico. This graphite is wholly amorphous and even under a high power microscope shows only shapeless articles.

The deposits are the result of the metamorphosis of coal seams by granite intrusives. An analysis of run of mine material shows 86.75 carbon, 7.6 silica, 0.65 iron oxide, and 5% aluminum.

Among graphite pencil leads which are used for drawing or writing, those having the softest black leads are those which have the higher percentage of graphite as compared with clay, whereas the harder leads have a greater proportion of clay. But the quality of a lead of given degree depends not only on the materials used but also the length of time in care and preparation and the compression to which they are subjected. Two parts by weight of graphite and three of clay, or equal parts of both, are considered good proportions for ordinary pencils. Of the very large number of different formulæ which are used, the following are given as examples:

Graphite	30 parts
Clay	9 parts
Grey antimony	9 parts
Tallow	1 part

The tallow is melted and added to the mixture which is then worked up in a lead mill. After baking, the leads are immersed in boiling wax. The following mixture is used for very hard drawing pencils:

Graphite	36 parts
Clay	18 parts
Grey antimony	8 parts
Lampblack	2 parts

The use of clay in pencil mixtures depends upon its property of hardening when heated, as well as its plasticity. The degree of hardness is somewhat dependent upon the temperature at which the leads are baked.

If baking has been conducted too rapidly, warping or twisting of the leads will result. When damaged in this

way they cannot be ground up and reburned. During baking, they are usually packed in some sort of carbonaceous packing material.

Other forms of carbon are sometimes used in connection with graphite to make leads that give a jet black mark. Among these materials are carbon black, lampblack, and occasionally almost all of the carbonaceous pigments.

CHAPTER XXVII

RESISTOR CARBON AND CARBON REFRACTORIES

MANY electric furnaces of the present day are of the resistance type. A number of these use granular carbon as the element through which the current passes and by the resistance of which the furnace is heated. Resistor carbon is ordinarily calcined material, petroleum coke, or anthracite coal screened to a uniform mesh. It can be made in practically all sizes but at the present time the standard sizes are those as given below. The first number indicates the screen mesh through which the material passes, and the second the screen on which it is retained. The $\frac{1}{4}$ " by $\frac{1}{8}$ " is the size in greatest demand.

Resistor Carbon Sizes:

$\frac{1}{8}$ " by $\frac{1}{16}$ "
 $\frac{1}{4}$ " by $\frac{1}{8}$ "
 $\frac{3}{8}$ " by $\frac{1}{8}$ "
 $\frac{3}{8}$ " by $\frac{1}{4}$ "
 $\frac{1}{2}$ " by $\frac{1}{4}$ "

The resistance of resistor carbon varies greatly, depending upon the size of the particles, their shape, the pressure if any, and the raw material from which it was made. The manufacturing processes it has undergone also vary the resistance. The values of the standard products, however, are quite constant under uniform conditions. The $\frac{1}{4}$ " by $\frac{1}{8}$ " size under a pressure of 620 grams per sq. in. at normal temperature has an average resistance of 0.810 ohms per inch cube, dropping to 0.230 ohms per inch cube at 1,000° C. The resistance without pressure is 1.800 ohms per inch cube at

room temperature and 0.600 ohms at 1,000° C. Of course, all resistor carbon will show the general property of resistance varying inversely with temperature.

In some cases waste electrodes or butts, the unconsumed portions of electrodes, are ground and screened for the manufacture of resistor carbon. As these materials have a high ash, their resistance is relatively high.

Resistor material may be manufactured to conform with higher or lower resistances than the figures indicated above. The possible variation is from 0.750 ohms per inch cube or slightly higher at room temperature, to as high as 2.75 to 3.0 ohms per inch cube.

Resistor carbon in its purest forms will run 59 to 98% carbon, and in its impure forms, as low as 75 to 80% carbon.

The amount of resistor used in a furnace varies decidedly with the type of furnace and the kind of operations in which the furnace is employed. Heat treating furnaces, the doors of which are frequently opened for longer or shorter periods with the possibility of entrance of air, use more resistor than brass melting furnaces or others of similar design which are naturally tightly closed at practically all times. Heat treating furnaces for iron, steel castings, and chain annealing and similar operations may use as high as 9 lbs. of resistor carbon per ton of metal treated. Brass furnaces, however, on the average will not consume more than a pound per day per 100 K.W. rated capacity.

As the resistor is oxidized by air, the ash remains in the troughs and gradually accumulates. The resistance increases with the increased ash content. New resistor carbon is periodically fed to the furnace but at times the ash content may rise to such a high value that the channel holding the carbon must be cleaned out. An entirely new charge of resistor is then placed in the furnace. Resistor carbon, to be entirely satisfactory in the usual commercial furnace, must have the following requirements: Its resistance must be as nearly constant as possible under varying temperature, for varying resistance reduces the power range of the furnace.

Its rate of oxidation should be as slow as possible thus reducing its consumption and repair and maintenance labor charges. It should have in addition as low an ash content consistent with its other requirements as can be secured to reduce the number of times the containers need to be cleaned.

CARBON REFRactories

Elementary carbon has a melting point assumed to be around $4,400^{\circ}$ C. It sublimes or volatilizes at approximately $3,500^{\circ}$ C. Inasmuch as its melting point is considerably above those of the normal metal oxides used for furnace linings except in oxidizing atmospheres, carbon is a very good refractory. It begins to oxidize between 500 and 600° C. In a reducing atmosphere it is better than any of the usual refractories.

For certain types of furnaces a current carrying bottom is required. The material largely used for this purpose is a mixture of ground carbonaceous materials with a binder like tar or pitch. The mass is tamped into place and baked, giving a hard product.

Some electrode manufacturers produce carbon paste as a commercial product. This is made of crushed calcined materials screened to a certain predetermined size and mixed with a proper amount of binding material. The binding material is varied according to the use to which the product is to be put. This material is sold in small lots, bagged for shipment or in carload quantities. Before use, it is heated to make it plastic.

Carbon blocks are generally used for furnace linings and furnace bottoms, particularly in large open furnaces or in places where greater structural strength is desired than would be formed by a monolithic lining. The blocks, being pre-formed and baked, are denser than the carbon paste and offer greater resistance to oxidation. Blocks are manufactured in practically all square electrode sizes. They are set up in the furnace like ordinary refractory bricks with the

exception that the bond used is carbon paste instead of refractory cement.

A number of standard shapes of the same dimensions as refractory bricks are marketed. The sizes follow, all dimensions being in inches:

9 by 4½ by 2½	Straight
9 by 4½ by 1¼	Split
9 by 4½ by 2½ by 2½ ₁₆	Wedge
9 by 4½ by 2½ by 1¾	Wedge
9 by 4½ by 2½ by 2½ ₈	Arch
9 by 4½ by 2½ by 1¾	Arch
9 by 4½ by 2½ by 1	Arch

These bricks and blocks are made of ground calcined coal or coke, bonded with tar and pitch, baked to a temperature high enough to completely coke the binder. Sizes other than those listed above are special, but practically any shape or size can be obtained.

The use of carbon refractories allows the possibility of having furnace linings able to resist temperatures at which our ordinary refractories would either melt, spall, or lose their valuable properties. Other than carbon, commercially we have no refractories useful above approximately 2,700° C.

CHAPTER XXVIII

CARBURIZERS

WHERE steel with a very hard surface is desired, as in gears, bearings, armor plate and similar products, a combination of hard exterior with a soft ductile core is obtained by introducing carbon into the skin or shell of the metal. Stock of 0.10 to 0.20% carbon is generally used and sometimes nickel steel, chrome steel or chrome nickel steel. Those elements which exist as double carbides favor the adsorption of carbon, e.g., tungsten, manganese, chromium and molybdenum, while those which form solid solutions, as nickel, silicon and aluminum oppose it.

Case hardening or carburizing materials may be solid, liquid or gaseous but the solid materials are used most extensively. The most important are various forms of charcoal, bone char, carbonized leather scrap, crushed bone, horn, mixtures of barium carbonate and charcoal or of various salts and carbonaceous materials. Barium carbonate and charcoal are more efficient than charred leather or wood charcoal.

There are on the market many so-called "secret mixture" case hardening materials. Extraordinary virtues are often claimed for these compounds. They are generally found to be chiefly mixtures of carbonaceous and cyanogen compounds possessing the well-known carburizing properties of these substances.

Commercial products are usually made by grinding the raw materials, mixing them together mechanically with organic binding materials, or in some cases silicates, drying and baking at low temperatures. Because of their effect on the steel, sulphur-bearing raw materials are usually avoided. Particular attention is paid to the screening and grading of

the raw materials to obtain certain granular characteristics and mechanical strength in the finished product.

Barium carbonate, when added to carburizers, increases the depth of carbon penetration over that obtained by wood charcoal. Small quantities are most effective. Hébert¹ states that charcoal alone case hardens to a degree which increases with the temperature. Addition of 10% sodium chloride retards carburization, as does 10% soda ash, but to a lesser degree. Potassium ferrocyanide is stated to be an accelerator at low temperatures. Rosin accelerates only at 800 to 900° C. At low temperatures pulverized bone acts as a retarder and from about 850° as an accelerator, while bone black acts as a retarder. It functions when used alone at a slower rate than does charcoal.

In the manufacture of steel, it is sometimes necessary, after decarburization, to raise the carbon content to a higher figure. This is done by means of high carbon ferro-alloys, pig iron, wash metal, carbonaceous materials and "carburite," a mixture of about 47-48% carbon, 28% steel and the remainder the bonding material. This product allows the introduction of carbon to steel in small definitely controlled amounts without the addition of other materials along with the carbon. Carburite, because of its high specific gravity, sinks below the slag on the surface of the steel, disintegrates quickly, making the time of adsorption very short, and makes certain almost complete adsorption of the carbon by the steel. Its use is increasing in steel manufacture.

¹ *Technique moderne*, vol. 18, pp. 481-91.

CHAPTER XXIX

PHYSICAL AND CHEMICAL PROPERTIES OF CARBON

FOR reference purposes the physical and chemical characteristics of carbon are tabulated below.

Atomic Volume	6.7 - 8.0	Petersen ¹
	11.0	Thorpe ²
Atomic Radii (Diamond)	0.77 Å	Pease ³
Boiling Point	3600° C	Violle ⁴
	4000° C	Crookes ⁵
	3500° C	Moissan ⁶
	3700° C	Mott ⁷
Compressibility (Diamond)	0.18 × 10 ⁻⁶ at 0 to 10,000 megabars pressure	Adams, Williamson and Johnston ⁸
(Graphite)	3.0 × 10 ⁻⁶ at 20° C at 100 to 500 megabars pressure	Richards ⁹
Cubical Expansion (Diamond)	580° - 0.00579 686° - 0.00785 750° - 0.01014	Joly ¹⁰
Dielectric Constant		
Diamond	16.47	Pirani ¹¹
Wood charcoal	2.4	
Dispersion Coefficient	0.0044	Boutan ¹²
Electrical Conductivity		
Diamond at 15° C	0.211 × 10 ⁻¹⁴ to 0.309 × 10 ⁻¹³ mhos	Artom ¹³
Graphite (Ag = 100)	0.00395 to 0.0693	Mathiessen ¹⁴
Electrochemical Equivalent	3	Coehn ¹⁵
Electrical Resistance		
Graphite, Ceylon	- 185° C - 0.00428 ohms per cm. cube - 66° C - 0.00335 " " " " 0° C - 0.00295 " " " " 21° C - 0.00283 " " " " 61° C - 0.00265 " " " " 89° C - 0.00254 " " " " 105° C - 0.00250 " " " " 191° C - 0.00220 " " " "	Königsberger and Reichenheim ¹⁶

Entropy of Carbon (Diamond)	25° C, 1 atm. P, 1.3	Lewis, Gibson and Latimer ¹⁷
Heat Emissivity		
Soot	100	Melloni ¹⁸
Lampblack	100	Favre and Silberman ¹⁹
Graphite	86	Petersen ²⁰
Heat of Oxidation		
Diamond to CO ₂	7824 cal. per gr.; 93.24 to 94.55 cal. per gr. atom	Favre and Silberman ¹⁹
Natural graphite to CO ₂	7796.6 cal. per gr.	
Artificial graphite to CO ₂	7762.3 cal. per gr.	Favre and Silberman ¹⁹
Cast iron graphite	7855 to 7865 cal. per gr.	Roth and Wallasch ²¹
Amorphous carbon to CO ₂	7912 cal. per gr.	Despretz ²²
Wood charcoal	8080 cal. per gr.	Favre and Silberman ¹⁹
Gas Carbon	8047.3 cal per gr.	Favre and Silberman ¹⁹
Acetylene black	7894 cal. per gr.	Mixter ²³
Heat of Sublimation	274 cal.	Gruneisen ²⁴
Heat of Transformation		
Graphite to diamond	0.5 cal.	
Amorphous carbon to graphite	3.04 cal.	
Amorphous carbon to diamond	3.34 cal.	
Heat of Vaporization	4086 cal. per gr. or 49,032 cal. per gr. atom 125 cal. per mol.	Smithells ²⁵ Thiel ²⁶
Index of Refraction		
Diamond	2.439	Newton ²⁷
Graphite	2.40242 to 2.45922	Walter ²⁸
Linear Expansion (Diamond)	1.93 to 2.07 - 38.8° C - 0.060000 0° C - 0.060562 10° C - 0.060707 20° C - 0.060857 30° C - 0.060997 40° C - 0.061142 50° C - 0.061286 40° C - 0.06118 40° C - 0.06119 580° C - 0.00193 686° C - 0.00265 750° C - 0.00338 0.0638	Gaubert ²⁹ Fitzeau ³⁰ Monckman ³¹ Röntgen ³² Joly ¹⁰ Joly ¹⁰
Graphite (Siberian)	17° C to	Muraoka ³³
Graphite	- 190° C - 0.04244	Dewar ³⁴

Magnetic Susceptibility

Diamond	$- 52 \times 10^{-6}$ mass units	Meyer ³⁵
Graphite at 18°	$- 8 \times 10^{-6}$ vol. units	Meyer ³⁵
Melting Point	over 3000° C	

Refraction Equivalent

Specific Electrical	about 5	Gladstone ³⁶
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Conductivity —

Graphite, various kinds	0.247×10^4 to	
-------------------------	------------------------	--

Electric light carbon

0.054×10^4 mhos	
--------------------------	--

Artom ¹³

Gas retort carbon

0.82×10^4 to	
-----------------------	--

Graphite electrodes at various temp.

0.385×10^4	
---------------------	--

Cellier ³⁷146.32 $\times 10^{-9}$ Cellier ³⁷

185.99×10^{-9}	
-------------------------	--

 $25^{\circ} - 100$ $400^{\circ} - 94.0$ $800^{\circ} - 81.5$ $1200^{\circ} - 66.0$ $1600^{\circ} - 65.0$ $2000^{\circ} - 68.0$ $2200^{\circ} - 69.0$ 0.147 Hansen ³⁸Favre and Silberman ³⁹

Specific Heat — diamond

 $- 50.5^{\circ} - 0.0635$ $- 10.6^{\circ} - 0.0955$ $10.7^{\circ} - 0.1128$ $140^{\circ} - 0.2218$ $247^{\circ} - 0.3026$ $606.7^{\circ} - 0.4408$ $806.5^{\circ} - 0.4489$ $985.0^{\circ} - 0.4589$ 0.20187 0.19702 Weber ⁴⁰Favre and Silberman ³⁹

Graphite, natural

 0.1138

Graphite, from iron

 0.1437

Graphite, natural

 0.1604 $61.3^{\circ} 0.1990$ $138.5^{\circ} 0.2542$ $201.6^{\circ} 0.2966$ $249.3^{\circ} 0.3250$ $641.9^{\circ} 0.4454$ $822.0^{\circ} 0.4539$ $977.0^{\circ} 0.4670$ $10^{\circ} 0.204$ $99^{\circ} 0.242$ 0.2608 0.2005 Weber ⁴⁰Regnault ⁴¹Regnault ⁴¹Regnault ⁴¹

Charcoal, wood

Charcoal, bone

Carbon, gas

Specific Volume

Graphite

Thermoelectric Force

Pt - C couple

 0.67 c.c. per g. Williams ⁴² $176 + 2.07 \Theta \text{ c.g.s. at}$ 0° Buchanan ⁴³

Pb - C couple	$390 - 1.87 \Theta$ c.g.s. at Θ°	Buchanan ⁴³
Transition Temperature		
Diamond to graphite	near 1500°	Doelter ⁴⁴
Vibration Frequency		
For red rays	39.88×10^{12}	Haber ⁴⁵
For violet rays	10.84×10^{15}	Haber ⁴⁵
Diamond	40×10^{12}	Wagstaff ⁴⁶
Graphite	27.7×10^{12}	Wagstaff ⁴⁶
Vapor Pressure		
	760 mm. at 3700° C	
	240 mm. at 3490° C	
	120 mm. at 3250° C	
	20 mm. at 2935° C	
	0.04 mm. at 2375° C	Thiel and Ritter ⁴⁷
	760 mm. at 4190° C	
	608 mm. at 4137° C	
	509 mm. at 4117° C	
	380 mm. at 4081° C	
	327 mm. at 4052° C	
	243 mm. at 4015° C	Kohn ⁴⁸

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